Reprinted in slightly modified form in "Coin World" Oct. 30, 1968 pp. 20, 23.

DETERMINING THE SILVER CONTENT OF COINS NON-DESTRUCTIVELY USING NEUTRON ACTIVATION ANALYSIS

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WHY NEUTRON ACTIVATION?

Historians concerned with the ancient and medieval worlds tend to rely solely on written evidence, neglecting the most abundant historical artifacts available - coins. When turning to numismatic evidence, the historian generally concerns himself only with the enscribed dates and names of rulers. However, the sheer quantity of coins available demands that the historian, and particularly the economic historian, study the coins for what they are - a money. In many cases coins are the most important, if not the only source of information about significant monetary and economic changes. Thus, the historian must go beyond the mere surface details of the coins, as valuable as these may be to him, and concern himself with the composition of the coins. In particular, this means a knowledge of the degree of fineness of the gold and silver issues. Although the fineness of gold coins can be approximated with reasonable accuracy by the simple method of determining the specific gravity of the coins, this is not a valid method for use with silver coins. The densities of silver and the common alloying metals, copper and lead, are numerically so similar that specific gravity measurements of silver coins frequently will not provide enough information to use in gauging the fineness of the coins.

The elemental composition of probably no more than 1000 ancient and medieval coins have been reported in the literature. The reason is obvious; the analysis of the composition of a coin meant the destruction of an irreplaceable object. Even the use of small scrapings for spectroscopic studies have been limited because of the reluctance of curators and collectors to allow any permanent damage to the coins.

X-ray fluorescence, the most common non-destructive methods of analysis, is of questionable value when applied to coins since only the surface is analyzed, and there exists the possibility of surface depletion of some of the metals. Neutron activation analysis (NAA), however, offers the possibility of making available to historians fundamental information about changes in the composition of coins without resorting to destructive methods

*Studies performed as part of doctoral research. Sept., 1967, address: Dept. of History, University of Washington of analysis. Since neutrons would penetrate through the coin it is possible to activate all parts of the coin and, as a result, any surface depletion effects would be unimportant. Yet very little research on coins has been done using this technique. Here, at The University of Michigan, we have developed a rapid, safe, and accurate NAA method of determining the silver content of coins using relatively inexpensive equipment of the type available in most colleges and universities.

The technique is relatively simple. A sample is irradiated with neutrons and made radioactive. Then the types and amounts of radioactivity in the sample are determined using radioactivity detection equipment. The types of radioactivity emitted by the sample provide unambiguous identification of the types of elements present in the sample. The amounts of radioactivity of each type found is related to the amounts of the elements which characterize the radioactivity emitted by the sample. For example, if a typical ancient or medieval silver coin was irradiated with neutrons in a nuclear reactor, the now radioactive coin would emit gamma rays and beta rays. The energies of these emitted rays could be examined and determined. A typical coin would be found to emit gamma rays having energies characteristic of radioactive isotopes of silver, copper and probably also tin, arsenic, gold, antimony, and zinc. From the intensities of these various gamma rays it would be possible to determine the percentage of silver, copper, tin, arsenic, gold, antimony, zinc, etc., in the coin. The method is non-destructive. The coin has not been harmed or altered in the process.

However, there could be one, perhaps major disadvantage. If the irradiation is performed using a nuclear reactor, the amount of radioactivity produced in the coin could be sufficiently great so that the irradiated coin would still be mildly radioactive for a number of months or years. To avoid producing any long-lasting radioactivity, we devised an irradiation procedure which results in the dissipation of the radioactivity within about 10-15 minutes. Our procedure only activates the silver in coins. As a result, we do not obtain information of the content of any element except that of silver. But the possible major disadvantage of residual radioactivity is eliminated and the coins we analyze can be returned promptly to their owners.

As described below, the method results in silver contents valid to about ±2%. The method is rapid; it only takes 2.5 minutes for an analysis. The method is safe; a small, movable, inexpensive neutron source is used rather than a nuclear reactor. The radioactivity detection equipment needed is available at almost every college and university. The analysis procedure is so simple that we have had undergraduates and even highschool students perform the analyses.

NEUTRON IRRADIATION

Two problems exist in irradiating silver coins. The first is concerned with the radioactive silver isotopes produced.

Each radioactive isotope has its own half-life, which is defined as the time-lapse required for half of the activity to dacay. For instance, when silver is irradiated with an intense source of neutrons, three radioactive silver isotopes are formed: ^{110m}Ag, ^{110}Ag, and ^{108}Ag; the half-lives of these isotopes are 270 days, 24 seconds, and 2.4 minutes, respectively. For ^{110}Ag this means that the activity would decrease to 1/2 of the original level in 270 days; in 2 × 270 = 540 days the activity would be down to (1/2) × (1/2) = 1/4 of that originally present. In 3 × 270 = 810 days the activity level would have decreased to (1/2) × (1/2) × (1/2) = 1/8 of that present originally, etc. Because of the long half-life of ^{110}Ag we wanted to avoid producing any detectable amounts of this isotope. The other two isotopes have half-lives so short that their activity is essentially completely decayed in 10-15 minutes. Production of the long-lived ^{110}Ag was avoided very simply. It was only necessary to irradiate the coins in a much less intense source of neutrons and therefore we chose not to use a nuclear reactor but instead used a small neutron source.

The second problem is much more difficult to solve. The amount of silver radioactivity produced in a coin is dependent not only on the amount of silver in the coin but also on the thickness of the coin. Unfortunately it is difficult to measure coin thicknesses accurately, and this is especially true for irregular shaped ancient and medieval coins. We were forced, therefore, to devise a method of irradiation and analysis which was independent of coin thickness.

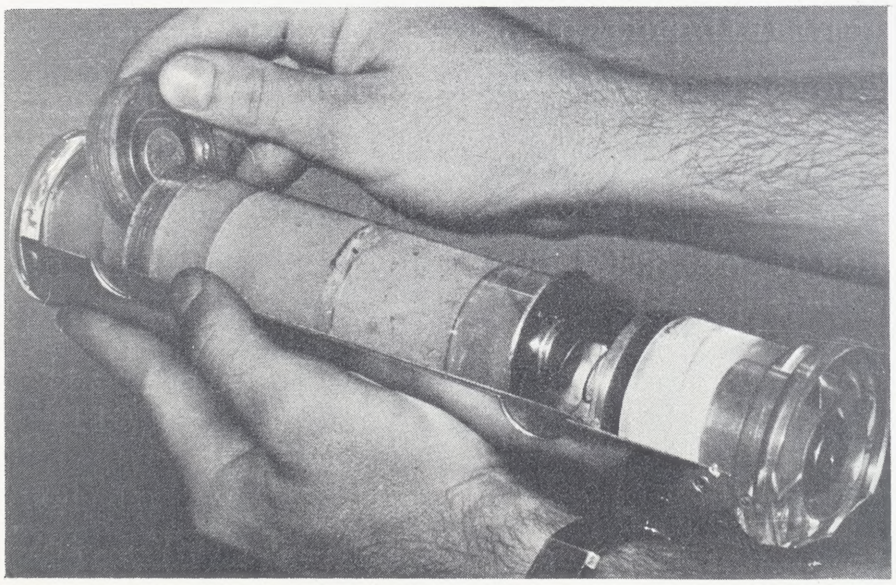


Fig. 1. A British 2-shilling coin with a U.S. 10¢ piece taped to the back of the coin is inserted into the irradiation holder.

A silver disk (of known weight) or a pre-1965 uncirculated U.S. 10¢ piece (90% silver) was taped to the back of the coin to be analyzed; this taped assemblage was inserted in a holder (see Fig. 1) and the holder inserted into a container housing the neutron source (Fig. 2).

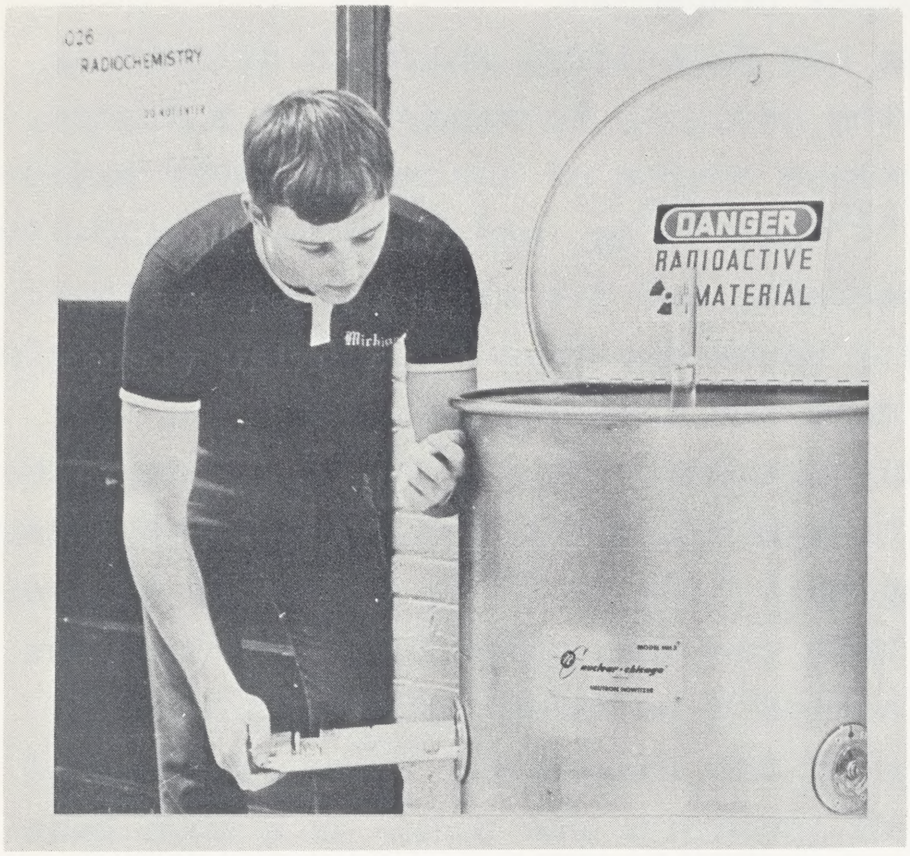


Fig. 2. The irradiation holder is inserted into the container housing the neutron source. The neutron source is composed of a mixture of plutonium and beryllium and is attached to the plastic rod which has been raised to align the neutron source with the irradiation holder.

The coin was left in this position for precisely one minute during which time it was bombarded by neutrons. The irradiation holder was then removed and the now slightly radioactive coin and disk were removed from the holder.

The coin and disk (or 10¢ piece) were then each placed near radioactivity detectors and the amount of activity in the coin and disk recorded for precisely one minute using nuclear counting equipment shown in Fig.3.

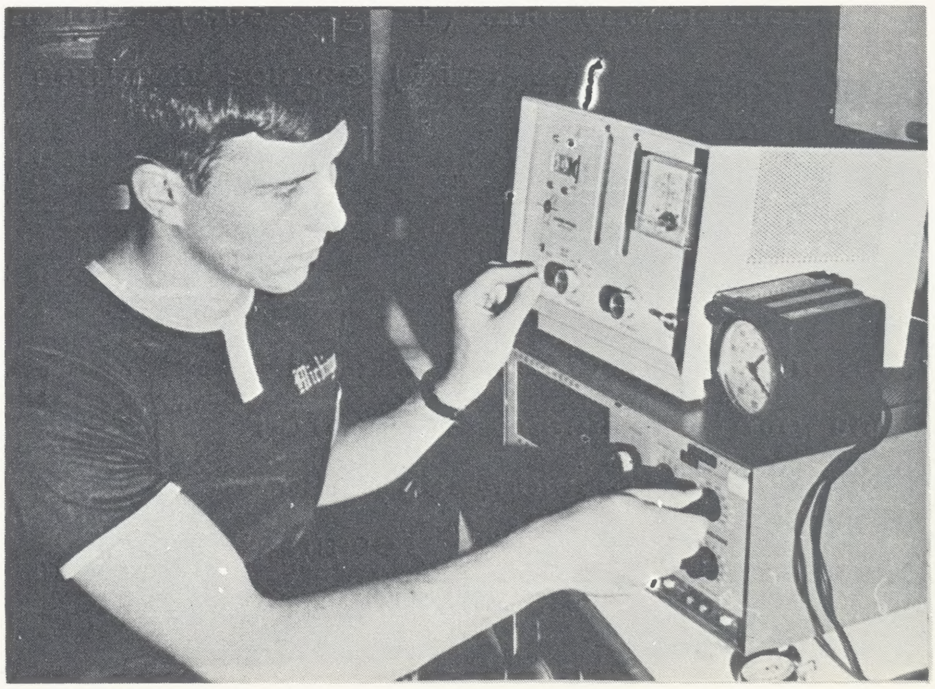


Fig. 3. The radioactivity of the irradiated coin and disk are recorded simultaneously using two scalers.

It was possible to transfer the coins and disk from the irradiation container to the detectors and reproducibly begin each activity determination 25 seconds from the end of each irradiation.

The following mathematical relationship was found to apply:

$$\frac{\text{Radioactivity in Coin}}{\left(\begin{array}{c}\text{Radioactivity in disk}\\ \text{or 10¢ piece}\end{array}\right)\left(\begin{array}{c}\text{Weight}\\ \text{of coin}\end{array}\right)\left(\begin{array}{c}\text{\% Silver}\\ \text{in coin}\end{array}\right)} = \text{a constant} \quad \text{Eq.(1)}$$

It is important to note that the thickness of the coin does not enter into this expression.

Table I contains data for various modern coins of known silver contents that were used in determining the value of the constant in the above equation; the average value of the constant, for our experimental set-up, was 0.371.

The equation above can now be used in a reverse manner to determine the silver content of an unknown coin. In this case, the equation becomes:

$$\text{\% Silver in coin} = \frac{\text{Radioactivity in Coin}}{\left(0.371\right)\left(\begin{array}{c}\text{Radioactivity in}\\ \text{disk or 10¢ piece}\end{array}\right)\left(\begin{array}{c}\text{Weight}\\ \text{of coin}\end{array}\right)} \quad \text{Eq. (2)}$$

Treating each of the coins listed in Table I as if it were a coin of unknown silver content we used Eq. (2) to calculate the silver percentage from the experimentally determined radioactivity data. These calculated silver percentages are also given in Table I and, as is seen from these data, the method results in experimentally determined silver purities that, on the average, are within 1-2% of the actual silver content.

An independent check of the method was made using a few Medieval Islamic coins. In this case the silver content was first determined by the neutron activation analysis method. Then the coins were dissolved in acid and the silver content assayed by a more accurate chemical method. These results, given in Table II, also show that the non-destructive neutron activation method of analysis results in silver contents that are within 1-2% of the true values.

To date, we have determined the silver contents of over 300 Islamic silver coins. Some of these are on display at the Kelsey Museum and others on display at the Alumni Memorial Hall of The University of Michigan. We are grateful to the American Numismatic Society and the Kelsey Museum for the short-term loan of some of these specimens.

Table I. Silver Analysis of Modern Coins

Coin	Weight grams	Thickness cm.	Const. Eq.(1)	Percent Silver Actual	Percent Silver By NAA
1961 Mexican 1 peso	15.92	0.198	0.380	10.0	10.2
1945 U.S. 5¢	4.99	0.173	0.354	35.0	33.4
1967 U.S. 50¢	11.50	0.175	0.364	40.0	39.3
1929 British 2 shilling	11.12	0.196	0.364	50.0	49.0
1925 Austrian 1 shilling	5.81	0.128	0.374	64.0	64.5
1944 Philippine 20 centavo	3.98	0.124	0.365	75.0	73.8
1951 Canadian 25¢	5.75	0.142	0.368	80.0	79.4
1886 Swiss 1 franc	4.78	0.122	0.372	83.5	83.7
1908 U.S. 25¢	5.69	0.127	0.384	90.0	93.1
1944 U.S. 50¢	12.39	0.183	0.378	90.0	91.7
1882 U.S. $1.00	26.13	0.234	0.380	90.0	92.2
1918 Canadian 25¢	5.61	0.130	0.372	92.5	92.7
		Average:	0.371	Average % Deviation:	2.1%

Table II. Analysis of Medieval Islamic Coins

Ruler	Mint	Approximate Date, A.D.	Percent Silver by NAA	Percent Silver by Chem. Anal.
Barsbāy	Damascus	1422-1437	86 ± 2	87.7 ± 0.2
Barsbāy	Damascus	1422-1437	89 ± 2	93.1 ± 0.2
Barsbāy	Damascus	1422-1437	91 ± 2	92.1 ± 0.2
Jaqmaq	Damascus	1438-1453	93 ± 2	93.5 ± 0.2

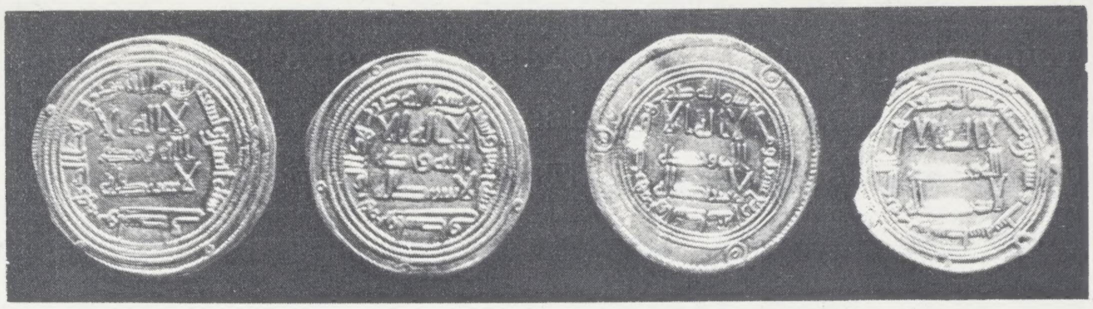
COINS ON DISPLAY IN KELSEY MUSEUM

The eleven silver coins on display in the Francis W. Kelsey Museum of Archaeology, The University of Michigan, represent three Muslim dynasties, seven rulers, three mints, and at least nine different dates. These dirhams are typical of the variety of sizes, weights, and styles one would encounter studying any field of numismatics. They are also important as they represent some of the variations in the fineness of silver coins. Although the purity of the dirhams on display fall into the range of medium to high degrees of fineness, very low percentages of silver have been determined in other Muslim coins.

The first four coins displayed were minted in the city of al-Wāsit by two Umayyad Caliphs, al-Walīd I (A.H. 86-96/A.D. 705-715) and Hishām (A.H.

105-125/A.D. 724-743). The purity of the coins is as follows:

Umayyad
Dirhams
(actual Size)

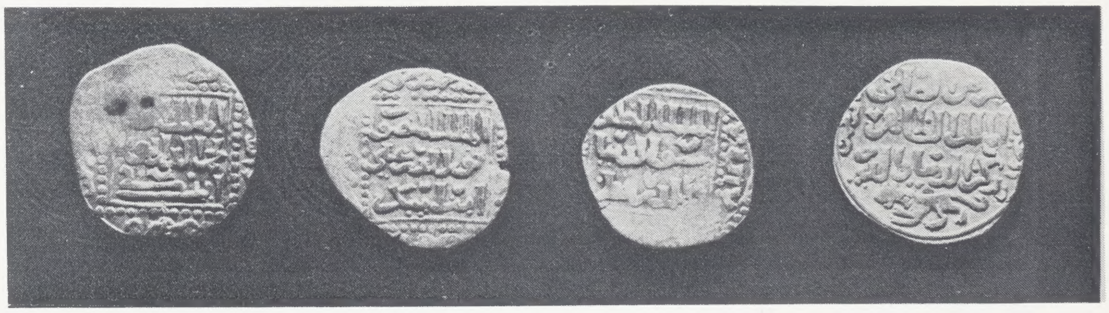


Ruler	al-Walīd	al-Walīd	Hishām	Hishām
Date	92 A.H.	96 A.H.	114 A.H.	126 A.H.
Mint	al-Wāsiṭ	al-Wāsiṭ	al-Wāsiṭ	al-Wāsiṭ
Purity	87%	90%	99%	96%
Weight, gms.	2.86	2.83	2.86	2.72

The purities of the above dirhams fall into two distinct classes associated with the two reigns. Al-Walīd's dirhams were issued only a decade after the monetary reform of the Umayyad Caliph ᶜAbd al-Malik and it is possible that the reformed Islamic dirham with its exclusively Arabic inscriptions was not as fine as our medieval sources would have us believe. On the other hand, the coinage of Hishām is almost pure silver indicating that he was economically in a position to issue the finest of silver coins.

The second set of coins represent the dirhams issued by the earliest Baḥrī sultans of Egypt: Aybak (A.H. 648-655/A.D. 1250-1257), ᶜAlī (A.H. 655-657/A.D. 1257-1259), Quṭuz (A.H. 657-658/A.D. 1259-1260), and Baybars I (A.H. 658-676/A.D. 1260-1277). All of the dirhams were minted in Cairo. Stylistically, the first three are a continuation of an Ayyūbid square-in-a-circle pattern while the Baybars' dirham breaks with tradition and includes a heraldic device, the lion passant. These coins are shown below.

Baḥrī
Dirhams
(actual size)

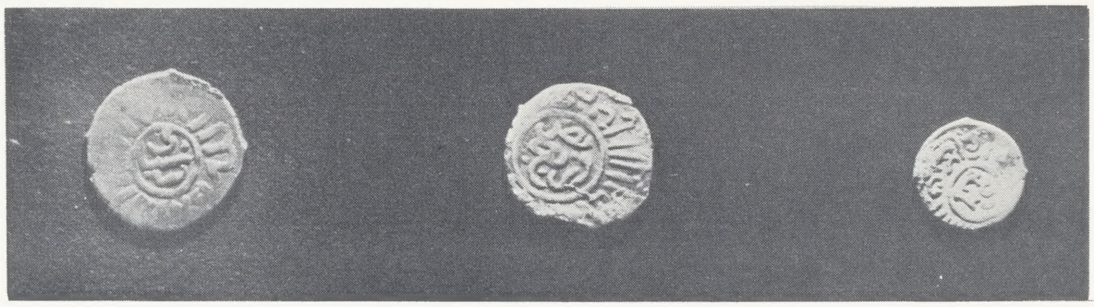


Ruler	Aybak	ᶜAlī	Quṭuz	Baybars
Date, A.H.	65-	655	657	669
Mint	Cairo	Cairo	Cairo	Cairo
Purity	69%	62%	57%	64%
Weight	2.81	2.81	3.00	3.05

In terms of size, these eight dirhams are similar; in fineness, however, there is a significant difference. The fifteenth century A.D. Egyptian historian al-Maqrīzī wrote that Baybars issued a silver coin which was 70% silver. The results of NAA tests support al-Maqrīzī's remark but the data also prove that a coin of roughly this purity was issued by the earlier Baḥrī sultans. While it is dangerous to conclude too much from these limited data, it does appear that the dirhams of Quṭuz were lower in silver than those of his predecessors or his successor. This debasement was a result of Quṭuz's need for large sums of money to pay for his expedition against the Mongols in Syria.

Debasements can take the form of a decrease in weight as well as a decrease in purity. The last group of dirhams represents this type of variation. Issued in Damascus by the Circassian ruler Barsbāy (A.H. 825-841/A.D. 1422-1437), these dirhams are much lighter in weight than the earlier dirhams. In fact, one of the coins has inscribed on it niṣf wa-rub^{c} which means three-quarters of a dirham coin weight or about 2.11 grams. The smallest coin has rub^{c} wa-thumn or three-eights of a dirham coin weight, ca. 1.05 grams, enscribed on it.

Circassian
Dirhams
(actual size)



Ruler	Barsbāy	Barsbāy	Barsbāy
Date, A.H.	--	--	--
Mint	Damascus	Damascus	Damascus
Purity	96%	95%	87%
Weight, gms.	2.02	2.04	0.83

The above table demonstrates that irrespective of weight and size, the NAA technique allows us to measure accurately the purity of silver coins. The range of values for Barsbāy's dirhams as determined by NAA is very close to that achieved by destructive analysis.

While all of these coins are only a small sample of the silver coins tested at The University of Michigan, they do represent the type of results one may expect to achieve using neutron activation analysis.

MAR., 1968, VOL. LXXVI, No. 3

RAPID NON-DESTRUCTIVE ANALYSIS OF THE SILVER CONTENT OF COINS USING NEUTRON ACTIVATION

By Adon A. Gordus, Ann Arbor, Michigan

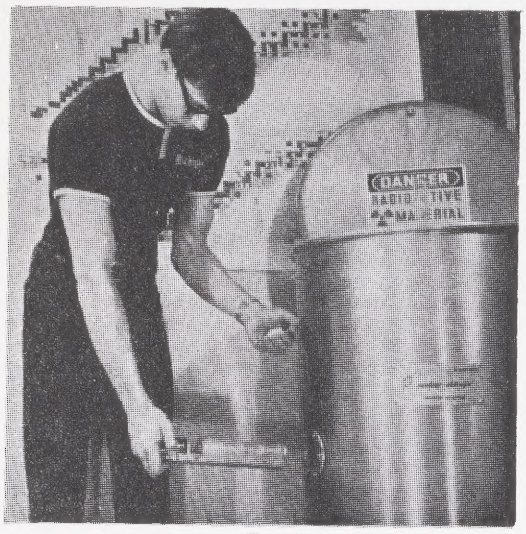


Fig. 1

The science of numismatics is concerned not only with the types, styles, weights, mint-marks, and dates of coins but also with the composition of the coins. Yet very little information is available on the elemental composition of ancient and medieval coins for the obvious reason that an analysis using chemical methods required destruction of the coins.

We have developed a means of determining the silver content of a coin using a non-destructive method of analysis. It is based on the neutron-irradiation of a coin to produce isotopes of radioactive silver. The coins are unharmed and there is no known scientific means of determining that the coins had ever been irradiated.

The method differs in two important respects from the usual neutron activation analysis procedures: (1) By using a relatively weak neutron source we avoid producing any detectable amounts of an isotope of radioactive silver having a half-life of 250 days. Only short-lived isotopes of silver are observed and the induced radioactivity decays completely in 10-20 minutes. (2) A typical activation analysis will result in reliable quantitative data only if the sample being irradiated is quite small. A typical coin is much too large and the calculated silver contents could be grossly in error. For example, by irradiating pre-1965 U.S. coins, all of which contain 90% silver, we could use data for a 10-cent piece to calibrate the irradiation-analysis procedure. Analysis of a 25-cent piece, a 50-cent piece, and a silver $1.00 would then indicate incorrect silver contents of 73%, 59%, and 43% respectively. We have devised a method of irradiation which compensates for such analysis errors.

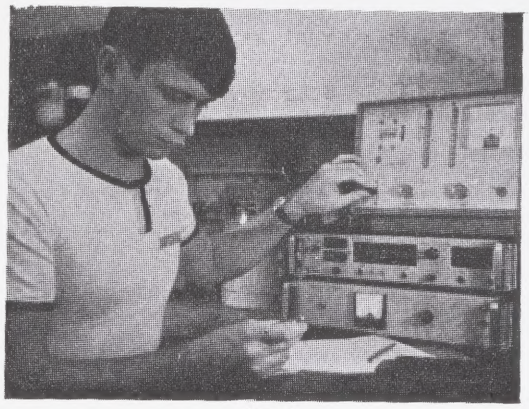


Fig. 2

We tape a small silver disk to the back of the coin and irradiate the coin and disk for one minute in a small neutron source as shown in Fig. 1. Because the neutron intensity is about 100 million times less than the neutron intensity in a typical nuclear reactor only silver, which readily absorbs neutrons, is made radioactive. The coin and the disk are then each placed next to radiation detectors and, 25 seconds after the end of the irradiation, the radioactivity in the coin and the disk is recorded for one minute, as in Fig. 2.

Using this procedure, we have found that the following equation applies:

$$\frac{(\text{radioactivity in coin})}{\begin{pmatrix}\text{radioactivity}\\ \text{in disk}\end{pmatrix}\quad\begin{pmatrix}\text{weight}\\ \text{of coin}\end{pmatrix}\quad\begin{pmatrix}\text{a numerical}\\ \text{constant}\end{pmatrix}} = \%\ \text{silver}$$

The numerical constant in the equation is determined by first irradiating coins of known silver content (various modern U.S. and European coins were used) and solving the equation for the numerical constant.

Usually the analysis of a coin is repeated about four or five times and the silver contents obtained in these determinations are then averaged. Table I is a list of a few contemporary coins analysed by this method. These data show that it is possible to determine the silver content of a coin to within an accuracy of about ±2%.

We have thus far analysed over 600 coins using this method. The majority of these were Mamlūk dirhams. Typical sets of data[1] from four reigns are shown in Fig. 3. Other coins include Sasanian and Arab-Sasanian dirhams, Umayyad dirhams, a hoard of 198 Ilkhānid dirhams of Uljaitu, and deniers tournois of Frankish Greece.

Besides providing data of interest to numismatists as well as economic historians, this method of analysis, because of its relative simplicity, is also useful in detecting certain types of forged coins. Among those coins we analysed we have found two that have abnormally low silver contents. One is a Sasanian dirham of Yezdegerd II (439-457 A.D.) having only 52% silver whereas others from his reign are about 90%. Another, a Mamlūk dirham of the Circassian Sultan Aynāl (1453-1461 A.D.) had only 8% silver whereas 12 other coins from his reign had contents between 84 and 97% silver. Probably both of these are ancient forgeries.

But we can also analyse for the silver content of coins made of other metals. For example, we have found that the presence of a few percent of silver in gold coins is readily determined. Thus, modern fakes of some ancient gold coins would be easy to detect since the silver content of the fake will undoubtedly differ markedly from that of the authentic gold coins.

A complete description of the analysis method and data on the silver contents of the various coins will be reported in separate publications.[2] Dr. George C. Miles of the American Numismatic Society, Dr. D. M. Metcalf of the Ashmolean Museum, and Dr. Jere L. Bacharach of the University of Washington Museum, have kindly arranged for the short-term loan of the coins which were analysed. Funds for this study were provided by the University of Michigan-Memorial Phoenix Project.

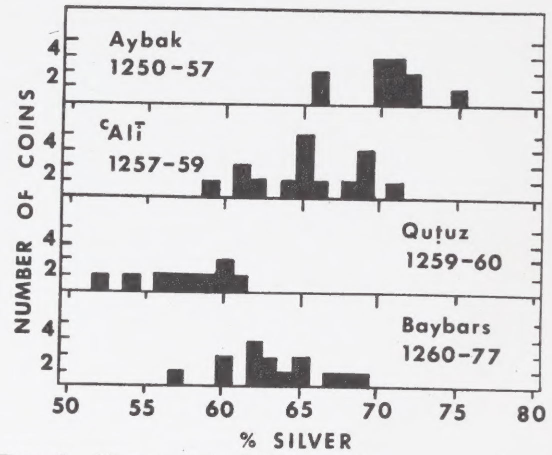


Table I. Silver Analysis of Modern Coins

	Coin	Percent Silver Actual	Percent Silver By NAA
1961	Mexican 1 peso	10.0	10.2
1945	U.S. 5c	35.0	33.4
1967	U.S. 50c	40.0	39.3
1929	British 2 shilling	50.0	49.0
1951	Canadian 25c	80.0	79.4
1964	U.S. 25c	90.0	90.2
1944	U.S. 50c	90.0	91.7
1882	U.S. $1.00	90.0	92.2

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[1] J. Bacharach and A. A. Gordus, J. Econ. and Soc. Hist. Orient, to be published (1968).

[2] Inquiries should be addressed to the author: Department of Chemistry, The University of Michigan, Ann Arbor, Michigan, 48104, U.S.A.

Neutron Activation Analysis of Almost Any Old Thing

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Certain archaeological artifacts, oil paintings, or even rare coins are irreplaceable not only for their artistic value but for their historical value as well. An archaeologist, for example, may find an object made of an exotic material not common to the area he is excavating. If he knew where the material came from, he then could establish the existence of contact between the two geographical regions. The historian, in examining the surviving written records of ancient or medieval cultures, has access to a large number of silver coins from these periods. Knowledge of the variation in silver content of these coins would provide him with important economic data. And, last, the director of an art museum must confirm the authenticity of a painting before committing funds to its purchase.

All of these research problems can be answered simply by determining the percentage of various elements in the mineral, coin, or pigment. But, because these treasures are irreplaceable, analyses must be such that they do not harm the object.

Neutron activation analysis can detect a number of elements with very great sensitivity in extremely small samples and, for this reason, is fast becoming the ideal method to use. A pinpoint speck of pigment from an oil painting or a small chip from an artifact can easily be analyzed. In cases where removing even a tiny sample would mar the object, as with a coin, the whole object can be analyzed nondestructively in such a way that it is impossible to tell that the object has been touched.

Activation Analysis

A sample is irradiated with neutrons by placing the object in a nuclear reactor or other source of neutrons. The neutrons penetrate the sample which absorbs some of the neutrons, resulting in the formation of radioactive isotopes. For example, sodium present in nature is in the form of sodium-23 with 11 protons and 12 neutrons in its nucleus. When the nucleus absorbs a neutron it becomes the isotope sodium-24 which is radioactive. The radioactivity associated with sodium-24 is unique to that isotope. It has a half life (time required to decrease radioactivity to half the initial value) of 15.06 hours and, when decaying to magnesium-24, emits gamma rays having energies of precisely 1.368 and 2.754 m.e.v. (million electron volts).

In most methods of activation analysis, a gamma-ray spectrometer is used to determine energies of gamma rays emitted by the irradiated sample. Gamma rays are high energy photons with typical energies around 1 m.e.v. The data from the spectrometer, therefore, can serve to identify the types of elements present. For example, if gamma rays of 1.368 and 2.754 m.e.v. are detected, it can be concluded that sodium is present in the sample.

The amount of an element present in a sample is calculated from intensities of the gamma rays emitted by the irradiated sample. These intensities are usually determined as the number of gamma rays detected per unit time and are typically reported as counts per minute (c.p.m.). In the irradiation of sodium-23, for example, only a small fraction, perhaps only one atom in every 10 billion, will be converted to radioactive sodium-24. But, for a given constant set of irradiation conditions, the number of atoms of an element converted to a radioactive isotope will be directly proportional only to the amount of that element present in the sample. Thus, if a chemical standard of known composition is irradiated together with the sample being analyzed, the amount of an element in a sample can be calculated as follows:

$$\frac{\text{Grams of element in the sample}}{\text{grams of element in the standard}} = \frac{\text{c.p.m. from element in the sample}}{\text{c.p.m. from element in the standard}} \qquad (1)$$

The sensitivity of detection for many elements exceeds that by other analytical methods, such as x-ray fluorescence, chemical precipitation (gravimetric), chemical titration (volumetric), and spectroscopic or electrochemical analysis. For some elements, such as iridium and indium, amounts as small as 10^{-12} gram can be detected, this being a sensitivity that is 10,000 times greater than that available by ordinary methods of analysis. On the other hand, certain elements cannot be detected at all by this method unless they are present in large amounts.

The factors that determine ease of detection are nuclear in origin. They include the probability that a given type of nucleus will absorb a neutron, as well as the rate at which the radioisotope decays. If the half life is less than a few minutes, extremely rapid techniques are needed to transfer the sample from the reactor to the gamma-ray spectrometer. Fluorine-20, with an 11.2-second half life, for example, is extremely difficult to detect. Conversely, if the half life is very long, typically greater than a few months or years, very few radioactive decays occur during the analysis period, making detection difficult.

Archaeological Obsidian Artifacts

Obsidian is a glassy mineral formed by rapid cooling of certain volcanic flows. The volcanic glass cleaves easily and permits fabrication of very sharp edged or tipped artifacts. The cultural group known as the Hopewell Indians, who inhabited what is now Ohio, Indiana, Illinois, and parts of Michigan and Wisconsin during the period 300 B.C. to 500 A.D., used obsidian for fabricating arrowheads and spearheads. Although these artifacts have been found in burial mounds, there is no evidence to indicate that these particular projectile points were ever put to use. But what makes these artifacts especially important to anthropologists is that there are no geologic sources of obsidian in the Hopewell region of the United States: The closest sources are in the western United States and in Mexico.

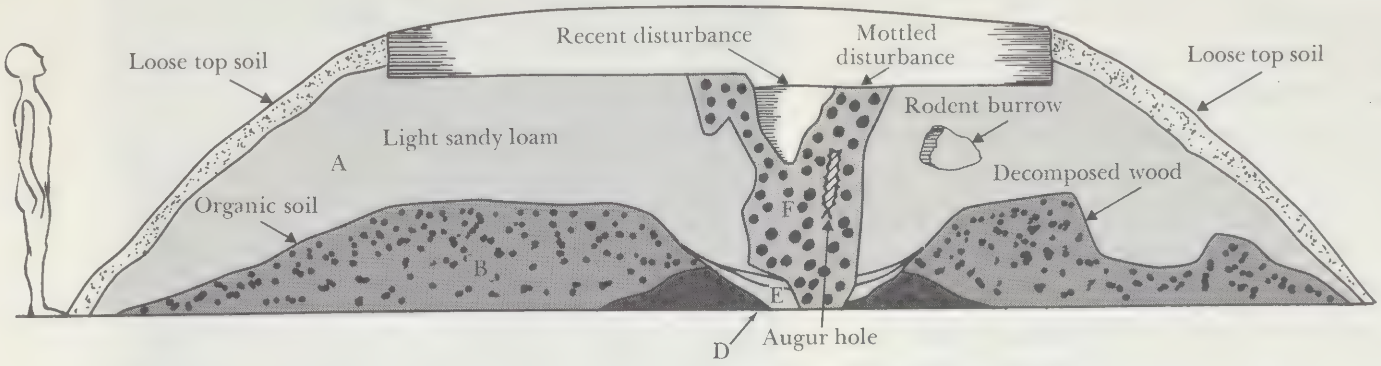
Excavations conducted by The University of Michigan at Hopewell burial mounds, Grand Rapids, Mich.

Medium-sized mound before excavation

View of mound after excavation showing burial chambers uncovered by diggers

Professor James B. Griffin, director of the university's Museum of Anthropology, examines skeletal remains and artifacts

Projectile point made from obsidian



Soil profile of a Hopewell Indian burial mound. A, mound fill; B, cap containing outlines of woven baskets for carrying earth; C, lens which is a layer of dark brown sand over entire burial area; D, floor; E, burial chamber; F, Coffinberry's intrusion

First Century A.D. Culture in Ohio

The Hopewell Indians were among the earliest to initiate trade and to help spread culture among prehistoric tribes. Their elaborate burial mounds, scattered over the southern part of Ohio, with the more spectacular in the Upper Great Lakes Region where they migrated, suggest an advanced culture and a well developed concern for the afterlife. The wealth of objects buried with the dead indicates domestic occupation, architectural practices, and both technology and skilled craftsmanship. A complex social organization can be discerned from the marked contrasts in ceremony and splendor of the burials.

Hopewell culture flourished between 300 B.C. and 400 A.D. in the Upper Great Lakes Region. Here the Hopewells established their largest ceremonial center in what is now Grand Rapids. Some 30 to 40 mounds still remain on the west and some 17 mounds on the east. This latter group, known as the Norton Mounds, represents a cultural peak, after which the quality and quantity of burial articles declined and the elaborateness of the mounds disappeared.

The Norton Mounds, rising 2 to 5 feet above the surrounding terrain, were first excavated in 1874 by W. L. Coffinberry, who called them "nearly homogeneous" and "hastily built." In 1915 they were again excavated by H. E. Sargent who described them more accurately. Sargent's conviction that the mounds were carefully structured was confirmed by James B. Griffin and Richard E. Flanders of the University of Michigan in 1963. They undertook a painstaking excavation which disclosed that all mounds were constructed according to the same definite plan—so careful a plan, in fact, that the diggers concluded it had to be an important and traditional part of the burial ceremony.

As the mound was originally constructed, from the top down, were found a surface of humus and sod, then the mound fill of sandy loam, then the cap with a central plug. The cap contained outlines of woven baskets for carrying earth, the basketloads of which were estimated at 500,000 for the mound shown here. Below this was a layer of ash—probably the remains of a canopy of branches—then a layer of black dirt thrown up from the burial pit.

Under the rectangular burial pits was a floor of widely spaced logs filled and covered with a light yellow sand with a "lens" of dark brown sand over the entire burial area. Bodies and burial goods were under the lens and upon the floor.

Grave goods were both practical and ornamental and included such objects as dishes, projectiles, tobacco, pipes, and imported luxury items. After excavation the mounds were restored to their original appearance, but the discoveries support the theory that the mounds were constructed about the first century A.D., a time described by anthropologist George Irving Quimby as "a climax of culture—a kind of classical period, the like of which was never achieved again." As sometimes happens, the culture may have been sacrificed for social improvements.

Therefore, if the geologic origin of Hopewell obsidian could be determined, valuable information on the cultural contacts of these Indians would be provided.

Fortunately, obsidian, unlike flint, is a fairly uncommon mineral. The number of major geologic obsidian sources in North America is less than 50, yet more than 50 analyses were required to identify the source of Hopewell obsidian. First it was necessary to determine whether the composition of obsidian from single geologic sources was relatively constant; this was found to be the case. Next, the elements which varied significantly between geologic sources were determined. These elements included sodium, manganese, iron, scandium, samarium, lanthanum, and rubidium, whereas silicon, oxygen, and aluminum vary little between sources.

When obsidian is irradiated for 1 minute in the nuclear reactor at the University of Michigan, most of the radioactivity observed immediately following the irradiation is due to aluminum-28 which has a half life of only 2.3 minutes. In about 30 minutes almost all of the aluminum-28 has decayed and for the next 20 to 30 hours more than 99% of the detected activity is due to two isotopes: sodium-24 (15.06-hour half life) and manganese-56 (2.58-hour half life). Because these elements serve partially to distinguish between sources, sodium and manganese analyses were routinely performed for all samples.

Ninety small chips of obsidian, each weighing about 20 mg., were individually sealed in polyethylene tubing and irradiated together with 10 chemical standard samples of known weights of $NaNO_3$ and MnO_2. The 100 irradiated samples were then placed in separate test tubes in an automatic sample changer equipped with a gamma-ray detector (Figure 1). A sample was automatically analyzed for 1 minute and removed from the detector; the next sample was inserted into the detector and analyzed, and the process continued automatically for about 22 hours. The counts were printed automatically on paper tape as the changer progressed to the next sample. A typical set of decay data for an obsidian sample is given in Figure 2.

Now it was only necessary to resolve the decay curve into its sodium-24 and manganese-56 decay components. For this operation the data were punched on IBM cards and a computer was provided with instructions for resolving the data for both obsidian samples and standards. Using Equation 1, the computer next calculated the grams of sodium and manganese in each sample, and sodium and manganese percentages were calculated from the weight.

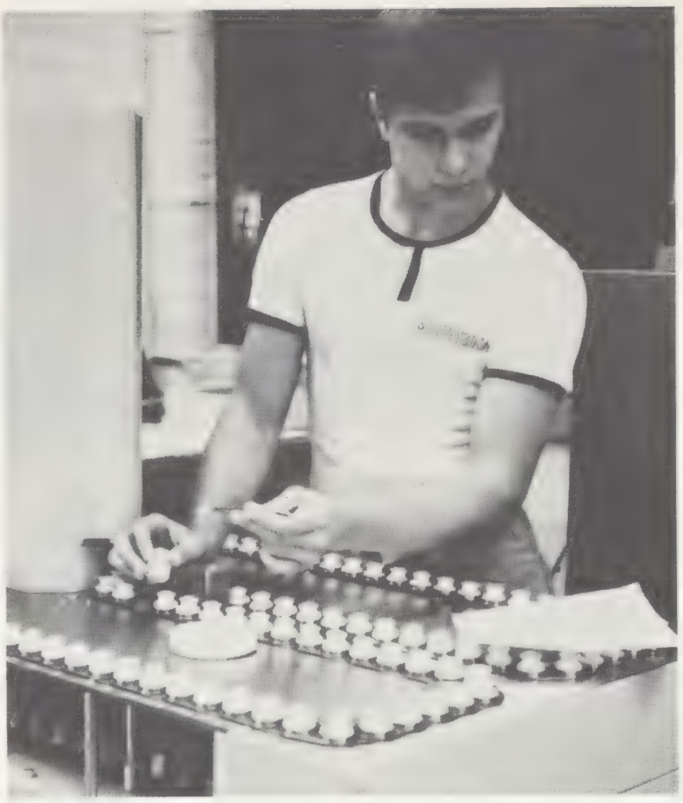


Figure 1. Irradiated obsidian samples placed in separate test tubes are moved automatically by the conveyor belt and analyzed every $2^1/_2$ hours

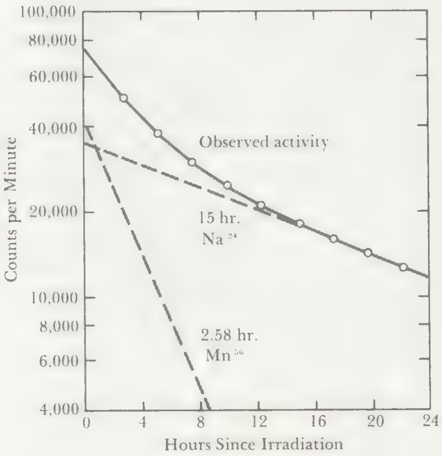


Figure 2. Decay data for an obsidian sample are a composite of two logarithmic-decay portions. The computer separates the decay curve into sodium and manganese components

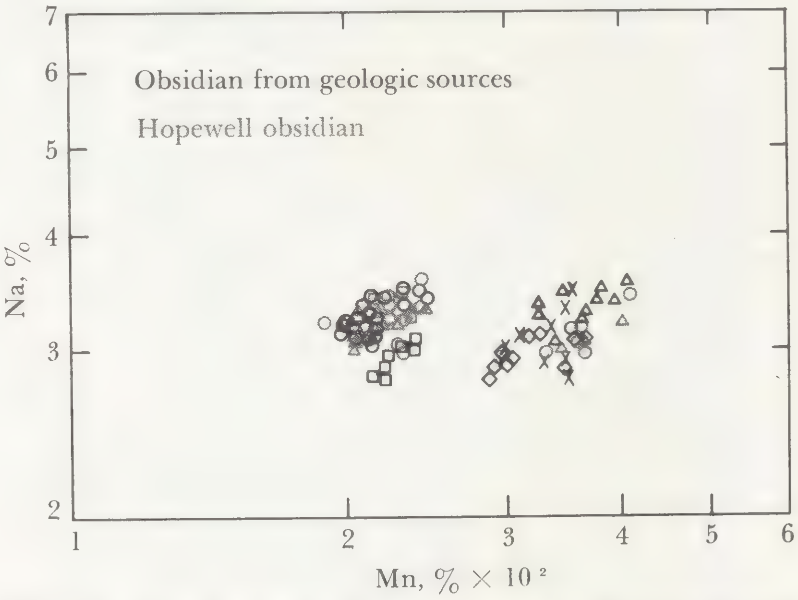


Figure 3. Data for the Na and Mn contents of obsidian artifacts found in Hopewell Indian burial mounds permit identification of source when compared with similar data obtained from samples collected from various geologic sources. Shown in color are data for Hopewell artifacts obtained from: Illinois, ; Ohio, ; Michigan, . In black are data for obsidian samples collected from: Yellowstone, ○; Oneida Perlite, Idaho, □; Mono Lake, Calif., △; Montana, ◇; and Wyoming, ×

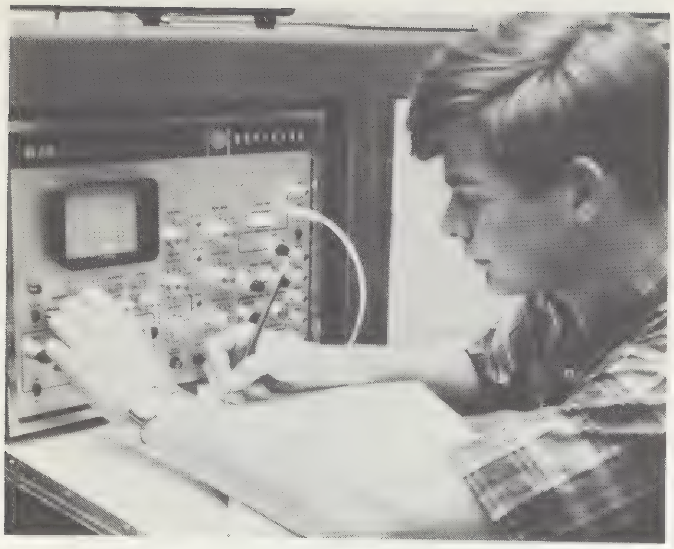


Figure 4. A multichannel gamma-ray spectrometer records spectra and the data are read out from "storage" of the spectrometer on punched paper tape

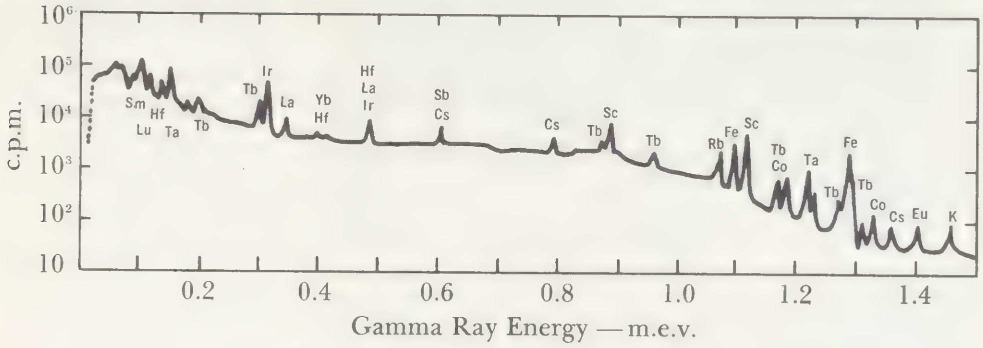


Figure 5. A typical gamma-ray spectrum, resulting from sample obtained from Obsidian Cliff in Yellowstone National Park, is composed of over 2000 points and indicates a variety of elements. Gamma-ray peaks are outlined for easy identification

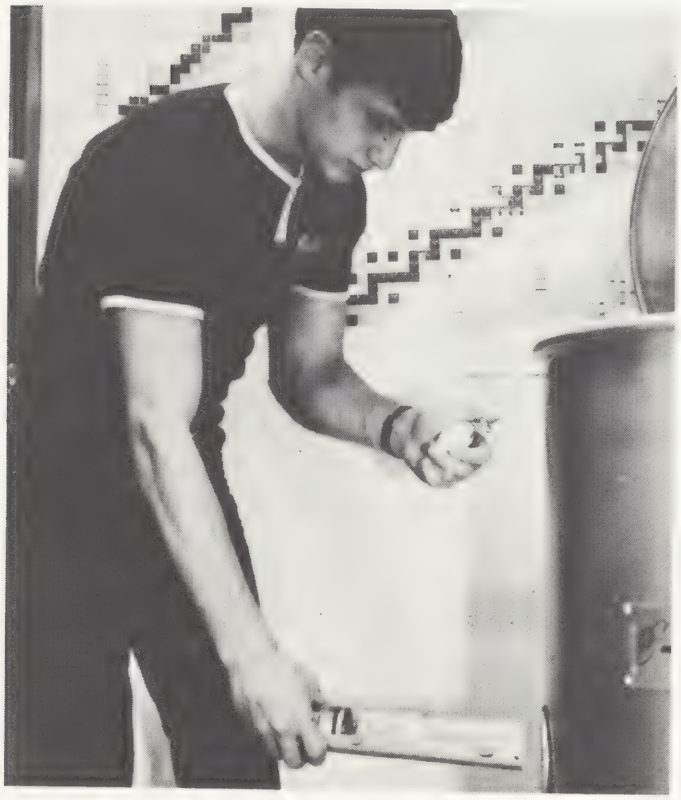


Figure 6. A sample holder containing the coin to be irradiated is inserted into the neutron source

This analysis procedure is particularly useful because it can be repeated as many times as desired with the same sample because the radioactivity in the obsidian dissipates in about a week. The samples can then be re-irradiated and repeat analyses obtained. Replicate analyses on the same samples give final average data which are valid to about ±5% of the average value. An accuracy greater than ±5% is difficult to obtain with neutron activation analysis; ±10 to 20% is more typical. This is one of the disadvantages of the method when highly precise analyses are needed.

The sodium-manganese data for obsidian samples from a number of geologic sources are shown in Figure 3, along with data obtained from artifacts found in Hopewell Indian burial mounds. Of the many North American obsidian sources tested (shown in black), only three have sodium and manganese contents corresponding to the cluster of data from Hopewell artifacts (shown in color at left). These are Yellowstone Park, Idaho, and Mexico. The smaller group of samples (in color at right) has sodium and manganese contents similar to those of a number of sources, including some shown here in black.

The problem, then, was to distinguish between these few possible geologic sources and determine which were the actual sources of Hopewell obsidian. The samples, therefore, were irradiated for 24 hours and additional isotopes, besides aluminum-28, sodium-24, and manganese-56, were produced in sufficient quantity for iron-59, samarium-153, lanthanum-140, scandium-46, rubidium-86, and about 10 or more other nuclides to be detectable. Because of the large number of gamma rays emitted by these samples, it was necessary to analyze them by gamma-ray spectrometry. To accomplish this, the radioactive obsidian samples were placed next to a gamma-ray detector which was electrically connected to a multichannel analyzer. The gamma rays which entered the detector were converted into electrical pulses whose voltage was proportional to the gamma-ray energy. The multichannel analyzer (Figure 4) is, in a sense, a small computer. It sorts and stores the electrical pulses according to the voltage of the pulses.

The data were now available as the number of gamma-ray counts (pulses) per gamma-ray energy increment. For instance, there may be 6690 gamma-ray pulses stored in the position corresponding to a gamma-ray energy range of 0.267 to 0.268 m.e.v., 6771 in the range of 0.268 to 0.269 m.e.v., and so forth. These data were fed out from the multichannel analyzer in the form of punched paper tape.

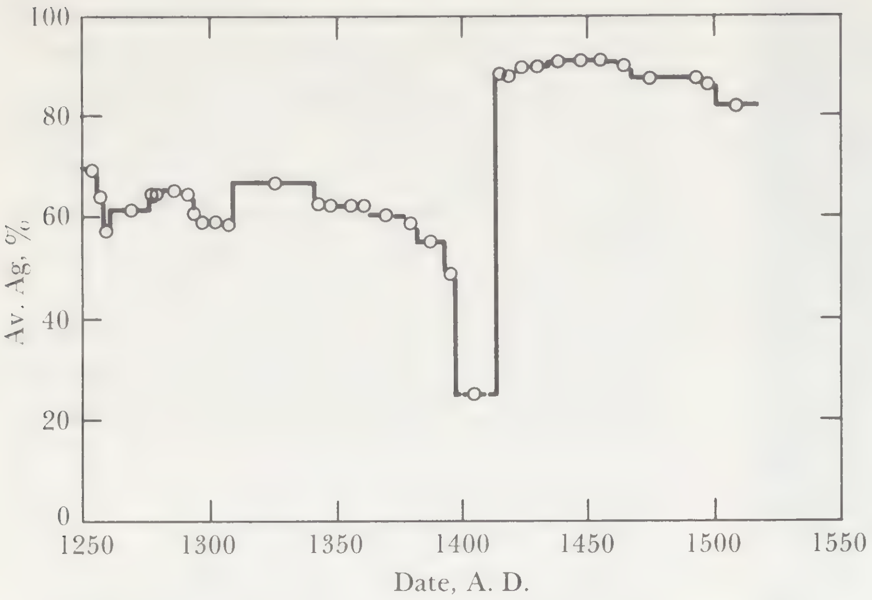


Figure 7. Medieval Islamic coins show marked differences in silver content during period from 1250 A.D. to 1500 A.D.

This punched tape was used in two ways. First, it was fed into a tape reader that types a copy of the number of counts per energy increment. Then the tape data were read into a small computer, which mechanically plotted a graph of the number of counts as a function of gamma-ray energy.

The gamma-ray spectra obtained (Figure 5) show various peaks, each of which corresponds to a gamma ray. The amounts of various elements present in the sample can be determined by first identifying the peaks, then measuring their size.

The Hopewell obsidian and various geologic samples were analyzed in this way. Most of the Hopewell obsidian gamma-ray spectra were identical with the spectrum in Figure 5, and the remaining Hopewell samples (Figure 3) were identical with another geologic sample of obsidian from another part of Yellowstone Park. It is significant that relative intensities of peaks of the gamma-ray spectra for Hopewell obsidian differed from those of samples from other geologic regions such as Mexico, Idaho, California, and Alaska. It could, therefore, be concluded that the Hopewell Indians obtained their obsidian from what is now Yellowstone National Park, thus solving the problem which has concerned anthropologists for 120 years.

Silver Coin Analysis

If silver coins are irradiated in a nuclear reactor for even a few seconds, the coins will remain slightly radioactive for a year or more because of the presence of a silver isotope with a half life of 270 days. Therefore, it was necessary to irradiate the coins in a much less intense beam of neutrons. A small neutron source composed of plutonium mixed with beryllium was used, and the coins were placed individually in a holder which was inserted into the container housing the neutron source (Figure 6). The neutron intensity in this unit is about 100 million times less than that in a reactor so that the only radioactivity detected was that due to two short half-life isotopes of silver—silver-108 (2.4 minutes) and silver-110 (24 seconds)—the radioactivity of which was dissipated in about 10 to 15 minutes.

In two half lives radioactivity would be $\frac{1}{4}$ the initial value, or $\frac{1}{2} \times \frac{1}{2}$; in three half lives it would be $\frac{1}{8}$ the initial value, or $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$

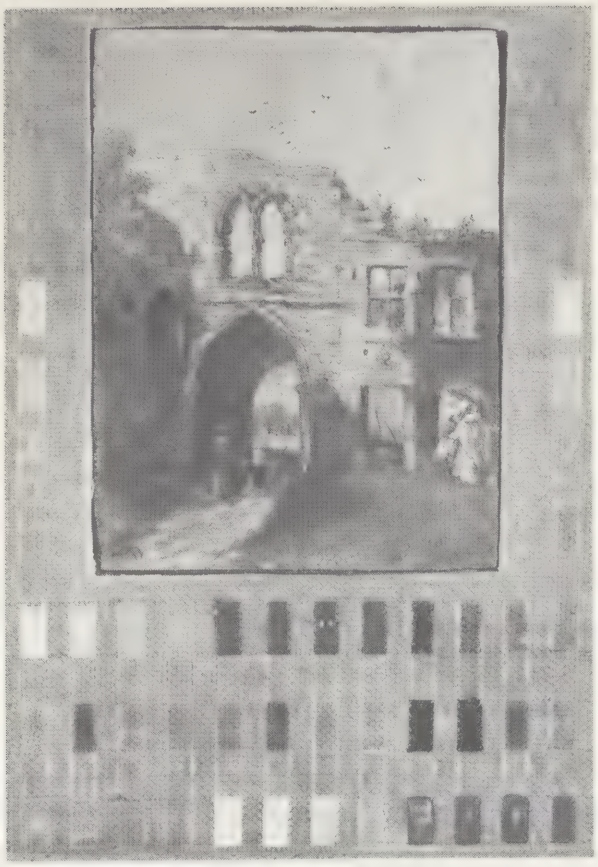
Silver, however, unlike most other elements, absorbs neutrons very readily and, for objects as large as a coin, the fraction of the neutrons absorbed depends on the thickness and silver content of the coin. For example, 212 c.p.m. were detected per gram of silver in a U.S. silver dollar (90% silver), but for a 10% silver Mexican peso, which is about the same size as a silver dollar, 480 c.p.m. were detected per gram of silver. Therefore, Equation 1 was not applicable and a new procedure of analysis was devised.

X-rays usually range from 0.005 to 0.1 m.e.v. and visible light about 10^{-6} m.e.v.

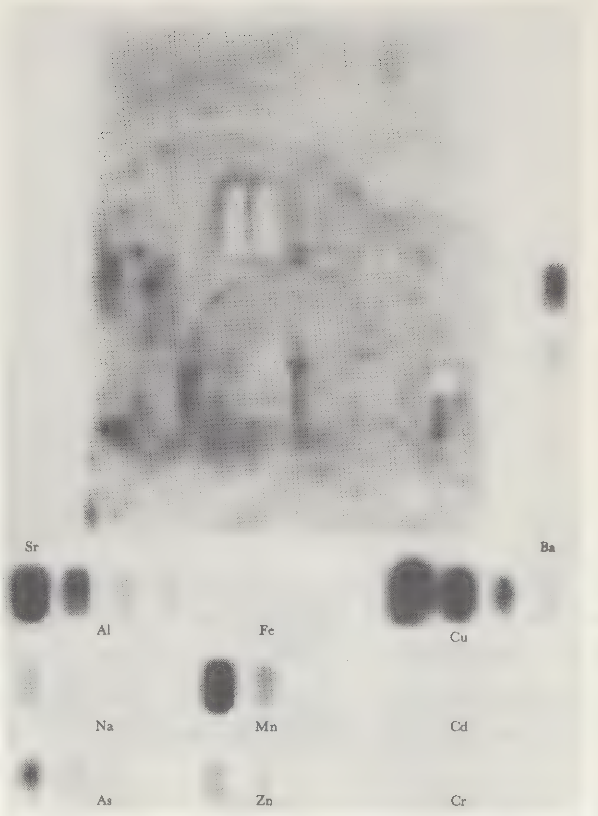
The method developed involved taping a pre-1965 uncirculated U.S. dime (90% silver) to the back of each coin and irradiating the two coins together for 1 minute in the neutron source. The silver radioactivity in both was then determined simultaneously using two detectors. The activity in the dime provided an indication of the amount of silver through which the neutrons had to penetrate to pass through the coin. But especially important was the fact that the counts per gram of silver in the coin divided by the counts in the dime were completely independent of either the silver content or thickness of the coin. Mathematically, this is written as:

$$\frac{\text{c.p.m. in the coin}}{\begin{pmatrix}\text{c.p.m.}\\ \text{in dime}\end{pmatrix}\begin{pmatrix}\text{weight of}\\ \text{coin, gram}\end{pmatrix}\begin{pmatrix}\text{\% silver}\\ \text{in coin}\end{pmatrix}} = \text{a constant} \qquad (2)$$

Coins of known silver content, such as U.S. 90% silver coins, the 40% silver Kennedy half dollar, a 35% silver 1945 U.S. nickel, as well as



a. A late nineteenth to early twentieth century oil painting on a wooden panel is placed on a standard pigment panel. Dress of girl at right is bright red

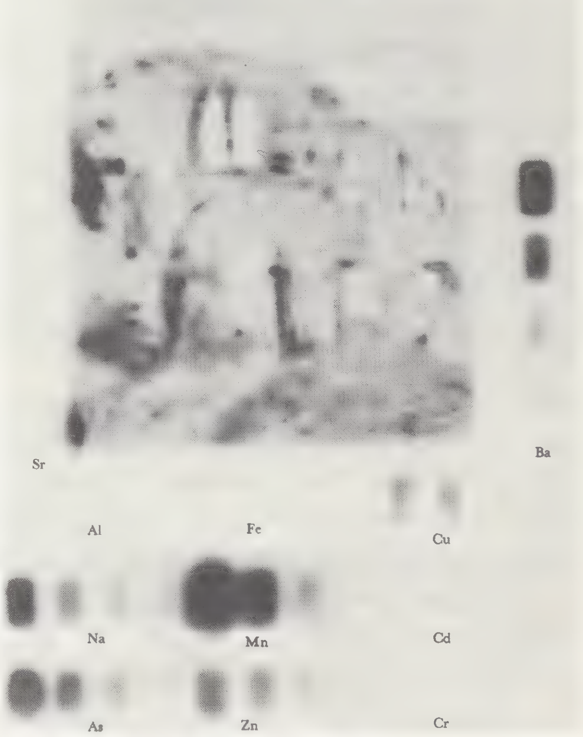


b. Autoradiographs of painting began 1 minute after activation. Density in dress is similar to that of activated aluminum (aluminum-28, 2.3-minute half life) on panel

various European coins, were used to determine experimentally the value of the constant for each set of detection equipment used. Each coin to be analyzed was weighed and irradiated with a dime; the activity was determined and the per cent silver calculated using Equation 2 and the average value of the constant previously obtained with U.S. and European coins.

This technique was also used to analyze a large number of medieval Islamic coins issued by the various sultans of Syria and Egypt. Figure 7, which shows the average silver content of these coins, points out the drastic changes in silver content of coins during this period. The economic historian can apply this information and correlate it with other information available. For example, in 1259 A.D., during the time the Mongols invaded Syria, the silver content decreased from 65 to 57%. Apparently the sultan ordered this decrease to pay the larger armies needed to fight the Mongols—who were eventually defeated. The increase from 59 to 67% about 1320 A.D. corresponds to the period during which the sultan and his armies invaded and conquered Armenia, thus acquiring access to rich silver mines.

It frequently happens that the decline of a culture is accompanied by a decrease in silver content of coins; this is first seen in the late 1300's. In the early 1400's, the economy was partially restored, but eventually underwent



c. Autoradiograph of painting 39 minutes after activation. No density appears in girl's dress, indicating that radioactivity of the activated isotope has expired. This suggests that the pigment contains aluminum, and is probably a rose madder lake which included an alumina mordant that was used during that period

Neutron activation with autoradiography can be used to identify pigments. The painting is first bombarded with neutrons, after which autoradiographs are taken at intervals; the radioisotopes are identified by comparison with those of a standard pigment panel

almost total collapse around 1500. The marked increase in silver content in the early 1400's was partially fictitious, however, because throughout that entire period, the weight of coins was being steadily decreased.

Paint Pigments

Perhaps the most challenging of the three problems discussed here is that of analyzing paint pigments from works of art. Extensive studies are underway with neutron activation analysis for determining both major constituents and trace elements of pigments. Some of these pigments are tiny specks of paint from oil paintings exhibited by major museums and others are raw paint pigments, identical in many cases with those used by artists over 300 years ago. Each sample is first irradiated, spectra of the type in Figure 5 are obtained, and the composition of the various elements in each pigment is determined.

After the data are compiled, the type and source of many pigments used in older paintings can be identified. This also aids in determining whether a painting was forged. A forger may be extremely skillful in duplicating the style of an artist, but he could not reproduce the precise composition of pigments used by the original artist. Also, determination of the mixture of pigments an artist used to achieve certain color combinations or effects aids the art historian and enables him to arrange an artist's paintings chronologically within his career because his pigments would vary according to sources obtained in the different regions where he lived.

One interesting art problem has already been solved by neutron activation analysis. A certain museum was interested in buying an expensive old painting composed of a number of sections of canvas sewn together. Art historians had suspected that a few of the sections had been added perhaps 200 years after the original had been painted. Neutron activation analysis of specks of blues and browns from each section indicated that the suspected additions were indeed painted with pigments differing from those of the authentic sections.

Neutron activation can be used to analyze almost anything. Pottery; copper- and ironware; gold, silver, and bronze coins and artifacts; ceramics; amber; sculpture; and old manuscript pages as well as inks used in their preparation all contain elements which can be identified. Their analysis can assist scholars in the humanities and social sciences without destroying the historic and artistic value of these objects.

Acknowledgment

The author wishes to thank all of the undergraduates for their assistance; James Griffin, director of the Museum of Anthropology at Michigan, who suggested the study of obsidian and who, along with his colleagues throughout the world, provided many of the samples; The American Numismatic Society and the Ashmolean Museum, Oxford, England, for silver coins; and The University of Michigan–Memorial Phoenix Project, the U.S. Atomic Energy Commission, and the National Science Foundation for their financial assistance.

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A reprint from Chemistry
Vol. 41, May 1968, Pages 8–15
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Activation analysis, artefacts and art

The extreme sensitivity of neutron activation analysis, coupled with the need for only very small samples, makes it the ideal technique for analysing precious artefacts, coins and paintings. From these analyses, a great deal of new information can be obtained about the cultures that produced the artefacts

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To museum curators, keepers of coin cabinets, and other guardians of ancient artefacts, the very sound of the phrase "chemical analysis" is distressing—and rightly so, for, until recently, an analysis frequently meant defacement or destruction of the ancient object. The desire to know more about the artefact and the society that made it was at constant war with another desire, equally strong, to preserve intact for posterity a unique object, of historical importance, and often great monetary worth as well. In recent years, this conflict has been resolved by the increased application of various non-destructive analysis techniques to problems in art, archaeology, and economic history.

These methods include various forms of X-ray analysis, electron microprobe studies, and neutron activation analysis (NAA). I have been particularly concerned with the use of this last technique in the study of artefacts, coins, and paintings.

The method of neutron activation analysis is relatively simple. A sample, which can be as small as a fraction of a milligram, is withdrawn from the artefact. The sample may be a minute pin-point speck of paint from a painting; it may be a tiny chip or flake unobtrusively removed from an archaeological artefact; it may even be an almost invisible streak of metal transferred from a coin or metallic art object to a small piece of etched quartz. The sample is then irradiated with neutrons, usually in a nuclear reactor, and the types and amounts of radioisotopes produced are determined using appropriate nuclear radiation detection equipment. From these data, the elemental composition of the artefact is determined.

Many elements are capable of being activated by neutron absorption. But what makes this method of analysis quite different from more conventional methods (such as X-ray fluorescence) is that the sensitivity of detection of a given element is dependent on nuclear properties. Thus certain elements such as oxygen, hydrogen, carbon, and nitrogen are not detected, whereas others such as copper, silver, gold, manganese, arsenic, and many of the rare-earths are very easily activated. This nuclear selection phenomenon has definite advantages in the analysis of artefacts, because it is usually the elements that are readily activated, many of which may be present only in trace quantities, which provide the greatest amount of information.

Interest in applying NAA to problems in the social sciences, humanities, and the arts has increased markedly in the last few years with the advent of the new lithium-drifted, germanium high-resolution gamma-ray detectors. It is very seldom necessary nowadays to perform time-consuming post-irradiation chemical separations in order to obtain gamma-ray spectra that can be interpreted accurately. Using semi-automated procedures and computer analyses of the data it is now possible to analyse easily thousands of samples per year.

The importance of analysing a large number of artefacts can hardly be exaggerated, because in most cases the answers which are sought depend upon the identification of discrete sub-growths, characterized by different elemental compositions, within a large group of artefacts. The crucial point at this stage of the investigation is a statistical one; when does a difference in elemental composition become statistically significant?

Tracking down the Indians

Similarities in the design and construction of artefacts are usually taken as an indication of the existence of trade between groups. However, elemental composition data showing that a common source of clay, stone, or metal was used in constructing the artefacts is a more direct form of evidence of cultural contact.

At the University of Michigan we have been involved in the analysis of prehistoric artefacts made of the volcanic glass obsidian. One problem which had confronted anthropologists for 120 years was concerned with a prehistoric North American culture known as the Hopewell Indians, who lived during the period 300 BC to AD 500 in the region that now comprises the states of Ohio, Michigan, Indiana, Illinois, and Wisconsin. Contained in the burial mounds they constructed were various artefacts and implements: pottery, shells, copper vessels, spear-heads and arrow-heads. A number of the projectile points were particularly interesting in that they were made of obsidian, a material not found geologically in the area of the United States occupied by the Hopewell Indians. The closest sources of obsidian were over 1500 miles from the Hopewell region, located in Mexico, New Mexico, and the western United States. Although this was evidence enough to indicate that prehistoric cultural contact extended over vast distances, it was important to know, if possible, which geological obsidian quarry sites were actually used, and thus determine the trade-route pattern that existed.

We performed two types of activation analyses. First, small samples of obsidian from artefacts, as well as geological source material, were irradiated for one minute in the University of Michigan reactor. For an irradiation of so short a duration only a few elements were activated sufficiently to be detected and, during the period 2-24h following

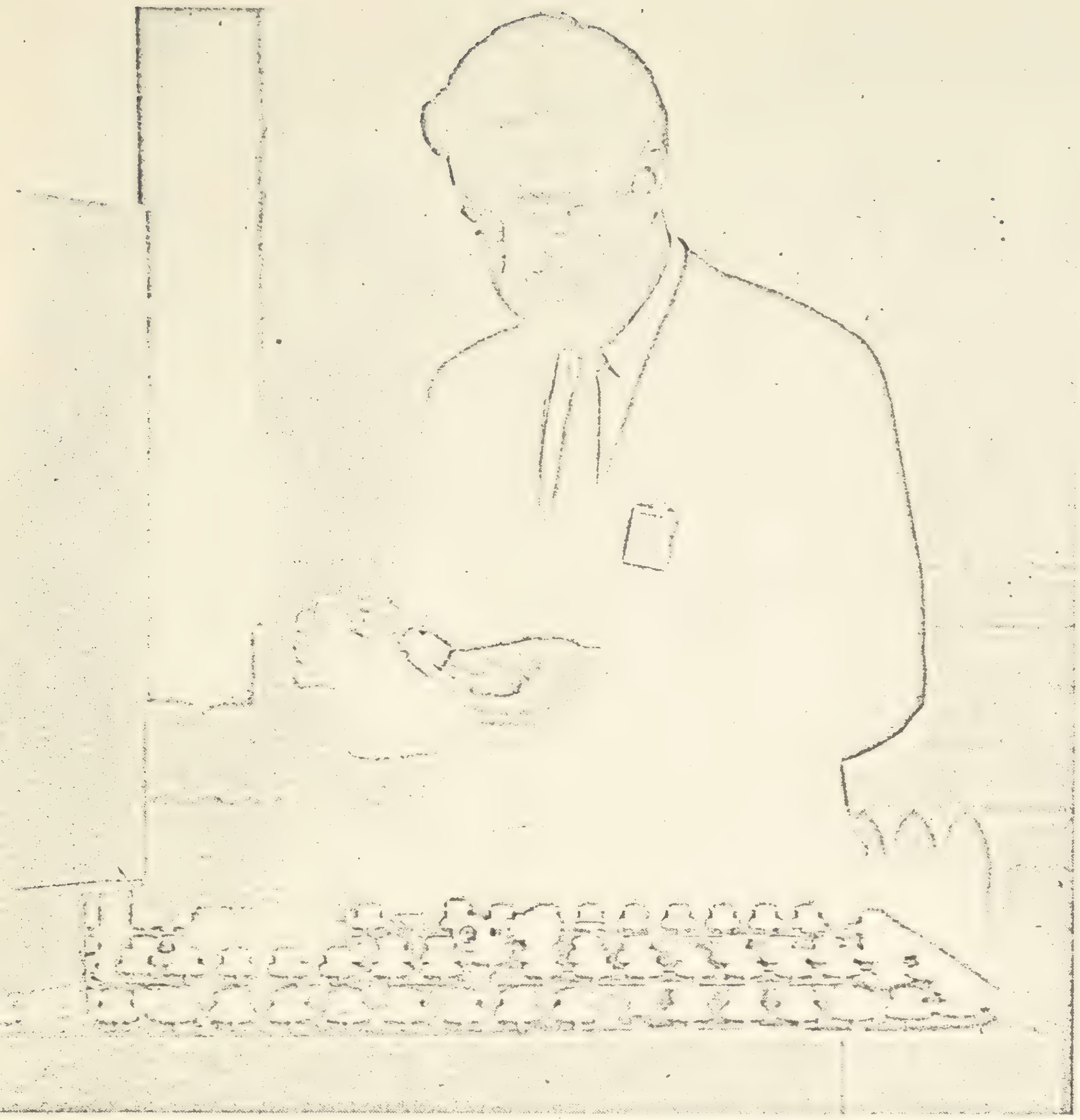

Figure 1 Professor Gordus placing reactor-irradiated samples of archaeological obsidian artefacts in test tubes. These samples are then automatically analysed over a period of 22h to determine the sodium and manganese contents

the irradiation, more than 99 per cent of the observed activity was due to the radioisotopes sodium-24 and manganese-56, which have half-lives of 15 and 2.6h, respectively. These samples (and sodium and manganese standards) were irradiated in groups of 100 and analysed by following the decay of each sample for 22h using an automatic sample changer (see Figure 1). We then analysed the decay data using a computer and calculated the per cent sodium and manganese for each sample.

These sodium-manganese data made it possible to eliminate most of the geological sources from further consideration, since only a few sources were found to have sodium and manganese contents that correspond to that in the Hopewell obsidian.

When we irradiated the obsidian samples for 24h, additional radioisotopes were formed in sufficient quantity to detect and it was possible to analyse for samarium, lanthanum, iron, rubidium, scandium, and at least 10 other elements by gamma-ray spectral analysis. The archaeological problem was solved when it was found that the elemental composition of the Hopewell obsidian was identical only with that of obsidian from a volcanic source in what is now Yellowstone National Park—a distance of 1600 miles from the Hopewell region of North America.

Over 2700 obsidian samples from geologic and prehistoric archaeological sites in Mexico, the United States, and the Near East have been analysed. These data are providing a clearer picture of the extent of prehistoric trade in these areas of the world.

Dating mediaeval hardship

The millions of coins housed in museums throughout the world comprise a valuable, virtually untapped source of information about the economic conditions of ancient and medieval societies. This is not to imply that historians have not used numismatic evidence in their research. Indeed, they have. But the numismatic studies have been limited to the examination of the designs, legends, mint-marks, dates, denominations, and weights of the coins. It is equally important to know what is in the coin.

Understandably, until a few years ago, probably no more than 500 coin analyses had been performed, since a chemical analysis meant the destruction of at least a portion of the coin. Even reactor-irradiation NAA determinations were undesirable since appreciable amounts of a 270-day half-life silver isotope could be formed.

During the last two years we have determined the silver contents of 1700 ancient and medieval coins using a simple NAA technique that uses a plutonium-beryllium source of neutrons that is 100 million times less intense than that available in a reactor. As a result, an undetectable amount of the long-lived silver isotope is formed, and only the short-lived silver isotopes silver-108 (2.4 min) and silver-110 (24s) are observed. The activity is dissipated in 10 to 15 min, and if repeat analyses are desired they can be performed the same day.

When using NAA to analyse objects as large and variable in size and content as a coin, errors will arise due to differences in neutron absorption and would result in data which are dependent on the coin thickness. To correct for such effects, small uniform-sized silver disks (or 90 per cent silver US 10 cent pieces) were taped to the back of each coin prior to irradiation. The silver activity induced in these disks was an indication of the amount of neutron absorption which occurred in the coin.

The induced silver activity in the coin per gramme of silver, divided by the silver activity in the standard disk, was found to be a constant independent of the thickness of the coin. After determining the numerical constant using modern coins of known silver content, it was possible to analyse ancient and medieval coins to determine the weight of silver and, hence, the silver content of the coins.

A single analysis required only 2.5 min: a one-minute irradiation, half-a-minute to transfer the coins and disk to separate detectors, followed by a one-minute counting period. Usually each coin was analysed eight to ten times in order to obtain an average value of the silver content valid to about ± one per cent.

Knowledge of the silver content of coins enables the historian who has no written records to establish the time and extent of debasement as well as reform of the coinage. Where documents are extant, the historian is able to determine the validity of the written sources which deal with the economic history of the period. Economic history is crucial to the study of any past civilization since the fluctuations in a money economy are the clearest and most sensitive indicators of changes in a society, whether social, political, demographic, or environmental.

Sasanian Persia (224 to 651 AD) is an example of a society which, despite its high development, is known to us only through very unsatisfactory sources. The only Sasanian evidence (excluding coins and objets d'art) are inscriptions; the literary evidence is peripheral to Persia itself since it is composed of Roman and Byzantine contemporary chronicles and later Arab histories.

No previous analyses of Sasanian coins had been made and it was generally assumed that all coins from this society contained 90 to 100 per cent silver. Preliminary data (see Figure 2) based on the analysis of over 300 Sasanian silver coins indicate that a number of periods were characterized by marked debasement and subsequent monetary reform. It is during these periods of debasement that the historian might expect to find that the Sasanians were at war or experiencing a famine or internal strife.

Additional historical studies of a more subtle nature can be made by determining changes in the silver contents of coins issued from various mints. For instance, data on Islamic coins from the period 700 to 740 AD show an increase in silver content from about 90 to 95 per cent for all mints except Al Andalus, the present-day city of Cordoba, Spain. The coinage from this mint was being decreased in silver during the same period and this dramatically illustrates the fact that Islamic Spain was fairly independent of the remainder of the Islamic Empire.

In recent months about 600 ancient coins were also analysed for gold, copper, arsenic, and antimony using a different activation-analysis technique. About 0.0001 g of a coin was transferred to a piece of etched quartz by streaking the quartz with the edge of the coin (see Figure 3). This piece of streaked quartz was then irradiated for two hours in the high-intensity neutron flux of the reactor. Enough radioactive gold, copper, arsenic, and antimony—as well as silver—was produced to permit the detection and determination of the relative amounts of these elements.

Figure 3 About 0.0001g of a coin is transferred by streaking a fresh surface on a piece of etched quartz. The streaked quartz is then irradiated in the reactor, and the composition of the streak determined

The relative amount of gold compared to silver in the coin streak was found to provide a good indication of the minimum number of silver sources used for various ancient coins. For instance, at least three different gold-to-silver ratios were represented by the Sasanian coins.

It was also found that modern fakes of ancient coins could frequently be detected by the fact that almost all of the modern fakes had abnormally low gold-to-silver ratios. Modern silver is highly purified and the traces of gold impurity in the silver ore are almost completely removed. The ancients, in all probability, did not even know that the silver they were using contained small amounts of gold.

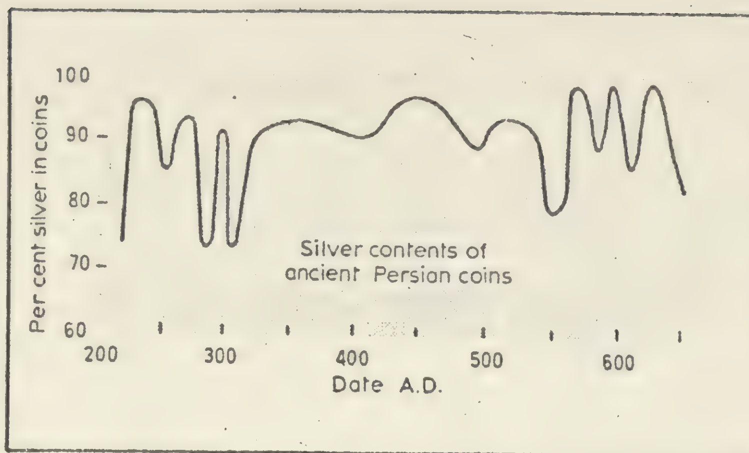

Figure 2 Preliminary analyses for the silver content of over 300 Sasanian coins indicate various periods of debasement and monetary reform.

Authenticating art

Analysis of paint pigments from works of art can provide information on the types and mixtures of pigments used by an artist. In some cases it may be possible to distinguish between similar pigments on the basis of differences in trace impurities. Such data would be particularly useful in authenticating works of art. But knowledge of the trace element contents of pigments, especially of those used in medieval times, would also assist in determining the trade-route patterns for the rarer pigments.

We recently analysed pigments from various Persian miniatures in a fifteenth-century edition of the Persian epic, the *Book of Kings (Shah Nameh)*. Microscopic samples weighing less than a microgramme were irradiated for four days in the reactor. From analysis of the gamma-ray spectra of these irradiated samples it was possible to determine that most of the red pigments were cinnabar (HgS), although some were mixtures of cinnabar and realgar (AsS). Similarly, the greens, although containing copper and therefore indicating verdigris (basic copper acetate), frequently also contained orpiment (As_2S_3).

Analysis of pigments from Spanish Monastery chant sheets of the same period indicated that whereas the red pigments also were cinnabar, they contained detectable trace amounts of lanthanum impurity. Thus, if further analyses support these initial observations it will be possible to distinguish between different geological sources of cinnabar.

The studies described above are only a small fraction of the types of analyses possible using neutron activation. Other studies being performed at laboratories throughout the world include analysis of ancient metal objects, ceramics, and glass, manuscript sheets and the inks and pigments used in their preparation, amber, and stone and metal sculpture. Indeed, virtually any ancient object can be analysed using this highly sensitive method.

STUDIES ON THE FINENESS OF SILVER COINS

BY

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Reprinted from / Tirage à part de :

**JOURNAL OF THE ECONOMIC
AND SOCIAL HISTORY OF THE ORIENT**

**JOURNAL DE L'HISTOIRE ECONOMIQUE ET
SOCIALE DE L'ORIENT**

VOL. XI / PART III 1968

E. J. BRILL / THE NETHERLANDS / LEIDEN

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INTRODUCTION

Historians concerned with the ancient and medieval worlds tend to rely solely on written evidence, neglecting the most abundant historical artifacts available—coins. When turning to numismatic evidence, the historian generally concerns himself only with the enscribed dates and names of rulers. However, the quantity of coins available demands that the historian, and particularly the economic historian, study the coins for what they are—a money. In many cases coins are the most important, if not the only source of information about significant monetary and economic changes. Thus, the historian must go beyond the mere surface details of the coins, as valuable as these may be to him, and concern himself with the composition of the coins. In particular, this means a knowledge of the degree of fineness of the gold and silver issues. Although the fineness of gold coins can be approximated with reasonable accuracy by determining the specific gravity of the coins, a method with which readers of this journal are already familiar [1]), this is not a valid method for use with silver coins, as is discussed below.

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[1]) Andrew S. Ehrenkreutz, "Byzantine Tetartera and Islamic Dinars," *JESHO*, VII (1964), 183-190. *Idem.*, "Studies in the Monetary History of The Near East in the Middle Ages," *JESHO*, II (1959), 128-181. See articles by the same author in *JAOS*, XXIV (1954) and *BSOAS*, XVI (1954) for further application of the method.

The elemental composition of probably no more than 1000 ancient and medieval coins has been reported in the literature. The reason is obvious; the analysis of the composition of a coin meant the destruction of an irreplaceable object. Even the use of small scrapings for spectroscopic studies has been limited because of the reluctance of curators and collectors to allow any permanent damage to the coins.

X-ray fluorescence, the most common non-destructive method of analysis, is of questionable value when applied to coins since only the surface is analyzed and there exists the possibility of surface depletion of some of the metals. Neutron activation analysis (NAA), however, offers the possibility of making available to historians fundamental information about changes in the composition of coins without resorting to destructive methods of analysis. Since neutrons would penetrate through the coin it is possible to activate all parts of the coin and, as a result, any surface depletion effects would be unimportant. Yet very little research on coins has been done using this technique. At the University of Michigan, we have developed a rapid, safe, and accurate NAA method of determining the silver content of coins using relatively inexpensive equipment of the type available in most colleges and universities.

Part I of this article is a description of the method including a comparison of the results of NAA with destructive analysis and specific gravity tests 1).

Part II is a report of the results of the application of NAA tests to Muslim dirhams (silver coins) issued by the Mamlūk rulers of Egypt and Syria, A.H. 648-922/A.D. 1250-1517. This chronological period was chosen as there were a number of coins available, tests by a destructive method have been published, and there were a number of contemporary textual references with which the numismatic evidence could be compared.

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1) For those who are interested in the technical details of neutron activation analysis, please write Professor Adon A. Gordus, Department of Chemistry, The University of Michigan, Ann Arbor, Michigan, 48104.

I. NEUTRON ACTIVATION ANALYSIS OF SILVER COINS *

The major value of neutron activation analysis is that the analysis can be performed without harming or destroying the specimen. The technique is relatively simple. A sample is irradiated with neutrons and made radioactive. Then the *types* and *amounts* of radioactivity in the sample are determined using radioactivity detection equipment. The *types* of radioactivity emitted by the sample provide unambiguous identification of the types of elements present in the sample. The *amounts* of radioactivity of each type found is related to the amounts of the elements which characterize the radioactivity emitted by the sample. For example, if a typical ancient or medieval silver coin was irradiated with neutrons in a nuclear reactor, the now radioactive coin would emit gamma rays and beta rays. The energies of these emitted rays could be examined and determined. A typical coin would be found to emit gamma rays having energies characteristic of radioactive isotopes of silver, copper, and probably also tin, arsenic, gold, antimony, and zinc. From the intensities of these various gamma rays it would be possible to determine the percentage of silver, copper, tin, arsenic, gold, antimony, zinc, etc., in the coin. The method is non-destructive. The coin has not been harmed or altered in the process.

However, there could be one, perhaps major disadvantage. If the irradiation is performed using a nuclear reactor, the amount of radioactivity produced in the coin could be sufficiently great so that the irradiated coin would still be mildly radioactive for a number of months or years. In the few cases where others have used this method for analysis of silver coins, their irradiations were carried out under conditions such that long-lived silver radioactivity was formed [1]). To avoid producing any long-lasting radioactivity, we devised an irradiation procedure which results in the dissipation of the radioactivity within about 10-15 minutes. Our procedure only activates the silver in coins. As a result, we do not obtain information on the content of any element except that of silver. But the possible major disadvantage of residual radioactivity is eliminated and the coins we analyze can be returned promptly to their owners.

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*) These studies were assisted by a grant from the University of Michigan-Memorial Phoenix Project.

1) H. Bluyssen and P. B. Smith, "Determination of the Silver Content of Greek Coins by Neutron Activation," *Archaeometry*, V (1962) 31-36. A. Ravetz, "Neutron Activation Analysis of Silver in Some Late Roman Copper Coins," *Archaeometry*, VI (1963), 46-55. Kurt Suber, *Neutron Activation Analysis of Roman Copper Coins from 250-500 A.D.*, Istanbul, Part I, Jan., 1965; Part II, May, 1966. M. J. Aitken, *et. al.*, "Neutron Activation Analysis of Ancient Silver Coins," *Conference on Radioisotopes in the Physical Sciences and Industry*, September, 1960, Copenhagen; *International Atomic Energy*, Vienna, 1962.

As described below, the method results in silver contents valid to about ± 2%. The method is rapid; it only takes 2.5 minutes for an analysis. The method is safe; a small, movable, inexpensive neutron source is used rather than a nuclear reactor. The radioactivity detection equipment needed is available at almost every college and university. The analysis procedure is so simple that we have had undergraduates and even high school students perform the analyses.

Neutron Irradiation

Two problems exist in irradiating silver coins. The first is concerned with the radioactive silver isotopes produced. Each radioactive isotope has its own half-life, which is defined as the time-lapse required for half of the activity to decay. For instance, when silver is irradiated with an intense source of neutrons, three radioactive silver isotopes are formed: ^{110m}Ag, ^{110}Ag, and ^{108}Ag; the half-lives of these isotopes are 260 days, 24 seconds, and 2.4 minutes, respectively. For ^{110m}Ag this means that the activity would decrease to $^1/_2$ of the original level in 260 days; in $2 \times 260 = 520$ days the activity would be down to $(^1/_2) \times (^1/_2) = {}^1/_4$ of that originally present. In $3 \times 260 = 780$ days the activity level would have decreased to $(^1/_2) \times (^1/_2) \times (^1/_2) = {}^1/_8$ of that present originally, etc. Because of the long half-life of ^{110m}Ag we wanted to avoid producing any detectable amounts of this isotope. The other two isotopes have half-lives so short that their activity is essentially completely decayed in 10-15 minutes. Production of the long-lived ^{110m}Ag was avoided very simply. It was only necessary to irradiate the coins in a much less intense source of neutrons and therefore, we chose not to use a nuclear reactor, but instead used a small neutron source.

The second problem is much more difficult to solve. The amount of silver radioactivity produced in a coin is dependent not only on the amount of silver in the coin but also on the thickness of the coin. Unfortunately it is difficult to measure coin thickness accurately, and this is especially true for irregular shaped ancient and medieval coins. We were forced, therefore, to devise a method of irradiation and analysis which was independent of coin thickness. A silver disk (of known weight) or a pre-1965 uncirculated U.S. 10-cent piece (90% silver) was taped to the back of the coin to be analyzed; this taped assemblage was inserted in a holder and the holder inserted into a container housing the neutron source. The coin was left in this position for precisely one minute during which time it was bombarded by neutrons from the neutron source, as shown in the sketch below. The irradiation holder was then removed and the now slightly radioactive coin and disk removed from the holder.

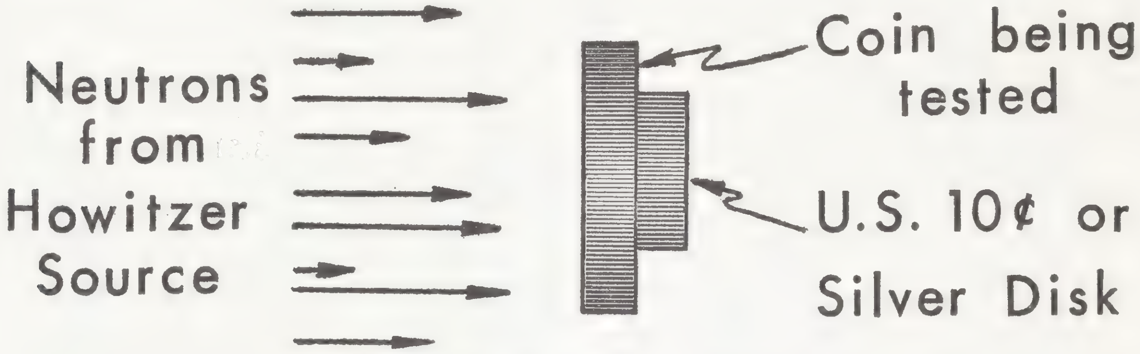

Fig. 1. Neutron irradiation of coin and disk

The coin and disk (or 10 cent piece) were then each placed near radioactivity detectors and the amount of activity in the coin and disk recorded for precisely one minute. It was possible to transfer the coins and disk from the irradiation container to the detectors and reproducibly begin each activity determination 25 seconds from the end of each irradiation.

The following mathematical relationship was found to apply:

$$\frac{(\text{Radioactivity in Coin})}{\left(\begin{matrix}\text{Radioactivity in disk}\\ \text{or 10 ¢ piece}\end{matrix}\right)\left(\begin{matrix}\text{Weight}\\ \text{of coin}\end{matrix}\right)\left(\begin{matrix}\text{\% Silver}\\ \text{in coin}\end{matrix}\right)} = \text{a constant}$$

Table I contains data for various modern coins of known silver contents that were used in determining the value of the constant in the above equation; the average value of the constant, for our experimental set-up, was 0.371, when a 10 ¢ backing coin was used.

The equation above can now be used in a reverse manner to determine the silver content of an unknown coin. In this case, the equation becomes:

$$\%\text{ Silver in Coin} = \frac{(\text{Radioactivity in Coin})}{(0.371)\begin{pmatrix}\text{Radioactivity in}\\ 10\text{ ¢ piece}\end{pmatrix}\begin{pmatrix}\text{Weight}\\ \text{of coin}\end{pmatrix}}$$

Treating each of the coins listed in Table I as if it was a coin of unknown silver content we used the above equation to calculate the silver percentage from the experimentally determined radioactivity data. These calculated silver percentages are also given in Table I and, as is seen from these data, the method results in experimentally deter-

TABLE I

Silver Analysis of Modern Coins

Coin	*Weight Grams*	*Thickness cm.*	*Const. Eq.* (1)	*Percent Silver Actual*	*By NAA*
1961 Mexican 1 peso	15.92	0.198	0.380	10.0	10.2
1945 U.S. 5 ¢	4.99	0.173	0.354	35.0	33.4
1967 U.S. 50 ¢	11.50	0.175	0.364	40.0	39.3
1929 British 2 shilling	11.12	0.196	0.364	50.0	49.0
1925 Austrian 1 shilling	5.81	0.128	0.374	64.0	64.5
1944 Philippine 20 centavo	3.98	0.124	0.365	75.0	73.8
1951 Canadian 25 ¢	5.75	0.142	0.368	80.0	79.4
1886 Swiss 1 franc	4.78	0.122	0.372	83.5	83.7
1908 U.S. 25 ¢	5.69	0.127	0.384	90.0	93.1
1944 U.S. 50 ¢	12.39	0.183	0.378	90.0	91.7
1882 U.S. $ 1.00	26.13	0.234	0.380	90.0	92.2
1918 Canadian 25 ¢	5.61	0.130	0.372	92.5	92.7
		Average:	0.371	Average % Deviation:	1.8%

TABLE II

Analysis of Medieval Islamic Coins

Ruler	*Mint*	*Approximate Date, A.D.*	*Percent Silver by NAA*	*Percent Silver by Chem. Anal.*
Barsbāy	Damascus	1422-1437	86 ± 2	87.7 ± 0.2
Barsbāy	Damascus	1422-1437	89 ± 2	93.1 ± 0.2
Barsbāy	Damascus	1422-1437	91 ± 2	92.1 ± 0.2
Jaqmaq	Damascus	1438-1453	93 ± 2	93.5 ± 0.2

mined silver purities that, on the average, are within 1-2% of the actual silver content.

An independent check of the method was made using a few medieval Islamic coins. In this case the silver content was first determined by the neutron activation analysis method. Then the coins were dissolved in acid and the silver content assayed by a more accurate chemical method. These results, given in Table II, also show that the non-destructive neutron activation method of analysis results in silver contents that are within 1-2% of the true values.*)

Specific Gravity Tests

The most common method of determining the purity of a coin, particularly gold and silver ones, has been to use its specific gravity in comparison with the specific gravity of a pure standard. The specific gravity test was known in the time of Herodotus and later to Archimedes who is credited with inventing the method. The medieval Arab scholars were also aware of the concept as were Europeans in the later Middle Ages.

Table III is a list of specific gravities of pure elements commonly found in coins.

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*) To date, we have determined the silver content of over 300 Islamic silver coins. We are grateful to the American Numismatic Society and the Kelsey Museum of The University of Michigan for the short-term loan of some of these specimens.

TABLE III

Specific Gravity of some Elements

Gold	(Au)	19.30
Lead	(Pb)	11.34
Silver	(Ag)	10.50
Copper	(Cu)	8.92
Iron	(Fe)	7.86

In order to calculate the specific gravity of the coin, the coin is first weighed in air and then weighed submerged in pure water with a temperature of about 25 degrees centigrade. The formula—weight in air minus weight in water divided into the weight in air—is used to determine the specific gravity of the coin. While there is the possibility of error in the weighing process, errors of a more substantial nature can result from the composition of the coin. Earle R. Caley, who has done the most research in the application of specific gravity for determining the purity of gold and silver coins, has listed some of these potential sources of error: a lack of knowledge of the mechanical and thermal history of the coin, serious foreign inclusions in the metal, hidden cavities, and a coin too light for accurate weighing. Two other potential sources of error exist—changes which take place according to the cleaning process used and a lack of knowledge of all the important elements in the coin when converting the specific gravity into a percentage of purity based on a table of the theoretical composition of the coin.

One basic method of coin debasement is to mix the pure metal with a base metal and claim the resulting coin represents the pure coin. Theoretically the mixture would have a specific gravity different from and usually less than the pure metal. In the case of gold coins this is true. If you mix any of the elements listed in the previous table with gold, the resulting mixture will have a specific gravity less than pure gold or 19.30. This means that specific gravity can be used to test the purity of gold and using a theoretical table devised by Caley it is possible to convert the specific gravity of a gold coin into a percentage of purity with only a one to two percent degree of error. Testing over 1000 Muslim dīnārs, Andrew Ehrenkreutz has demonstrated the practical use of specific gravity testing for pinpointing changes in purity as well as the high degree of purity maintained by most Muslim rulers [1]).

Caley has also established a series of tables to convert the specific gravity of silver coins into degrees of fineness [2]). His tables assume that silver is debased with copper which has a lower specific gravity than silver and the resulting mixture will have a specific gravity lower than 10.50. Tests have proven that Muslim coins include lead which has a higher specific gravity than silver. Thus it is possible for a very debased silver coin to have a specific gravity of 10.50 or even higher depending upon the percentages of lead and copper used in the debasing. In his chemical analysis of ten Muslim dirhams, Caley found a variation of 5% to 61% between the estimated silver content based on the specific gravity and the actual silver content [3]). Although the range of variations between the purity of Mamlūk dirhams as determined by NAA in comparison with estimates of the fineness of the silver coins based on specific gravity tests did not differ by as much as Caley's results, they demonstrated the dangers of using the older method.

From Table IV it is evident that the specific gravity test cannot be used to determine the purity of a single specimen, although it is possible that the specific gravity of one group of coins, such as those of Barqūq, will fall into a particular range of values which differs significantly from another group of silver coins and one can conclude that their respective compositions differ.

In conclusion, the neutron activation method of analysis allows the historian to determine within a few minutes if a coin is real or plated. By repeating the analysis a few times there are enough data available to

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1) See note 1, page 300.

2) Earle R. Caley, "Chemical Composition of Parthian Coins," *American Numismatic Society Numismatic Notes and Monographs No.* 129, New York, 1955.

3) *Ibid.*, "Chemical Composition of Some Early Dirhams," *A.N.S. Museum Notes*, VII, 1957, 211-217.

TABLE IV

A Comparison of the Percentage of Silver as determined by Specific Gravity Tests and NAA

Muslim Dirhams	*Percentage of Silver*	
Ruler	*NAA*	*Spec. Grav.*
Barqūq	64	67.5
Barqūq	48	34.0
Barqūq	27	under 25.0
Barsbāy	86	98.5
Barsbāy	97	100.0+
Qāyitbāy	89	82.0
Qāyitbāy	83	56.5

permit an estimation of the purity of the silver coin to a high degree of accuracy. The safety and speed of the method means that rare coins can be tested without fear of damaging them in any way. It is not even necessary to clean the coin as the method does not rely on the nature of the surface of the coin. The second part of this article demonstrates the application of the method to the historical period of Egypt and Syria known as the Mamlūk period, A.H. 648-922/A.D. 1250-1517.

II. SILVER CONTENT OF MAMLUK DIRHAMS *)

The specific historical period chosen for the first intensive study of the use of neutron activation analysis was the Mamlūk rule of Egypt and Syria, A.H. 648-922/A.D. 1250-1517. There were a number of advantages in choosing this era of Islamic History: (1) a significant number of dirhams are available for testing, (2) there are contemporary textual references with which the NAA tests can be compared, and (3) the results of cuppelation (destructive) tests on a number of Mamlūk dirhams have been published [1]). Using a destructive method of analysis, Dr. Paul Balog was able to establish the general pattern for the fineness of Mamlūk silver coins. The data from NAA tests support his conclusions as well as aid in pinpointing variations within the pattern and the specific periods when major changes occured.

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*) Further details can be found in the PhD dissertation of J. L. Bacharach, The University of Michigan, 1967, available through University Microfilms, Ann Arbor, Michigan.

As emphasized in Part I, the use of neutron activation means that no permanent change occurs in the coin and even very rare specimens can be safely tested. This is demonstrated by a comparison of the number of sultans represented in the tests by Balog and at The University of Michigan. Dr. Balog very generously donated, for destructive analysis, 54 Mamluk dirhams representing nine Baḥrī sultans (648-784/1250-1382) and four Circassian rulers (784-922/1382-1517). Our sample included 157 specimens representing 12 Baḥrī and 12 Circassian sultans. In an attempt to avoid duplicating Dr. Balog's work only the coins of seven sultans were represented in both tests and for three of these Dr. Balog had analyzed only one coin.

The general pattern of the fineness of Mamlūk dirhams is that the Baḥrī dirhams were about $66^2/_3\%$ silver. This degree of purity is reflected in an average exchange rate of one dīnār to 20 dirhams. When the Baḥrī period is analyzed in depth, certain variations begin to appear. The accompanying chart represents the spread of values for the first four Baḥrī sultans: Aybak (648-655/1250-1257), ʿAlī (655-657/1257-1259), Quṭuz (657-658/1259-1260), and Baybars I (658-676/1260-1277). Although the values for the coins fall into a fairly wide field, they do exhibit a certain pattern. The dirhams of Aybak are about 70%, those of ʿAlī drop to 65%, then to around 57% for Quṭuz and finally a return to the 60's for Baybars. The model for these Baḥrī issues in terms of style and fineness was the Cairo issues of the last major Ayyūbid ruler, al-Ṣāliḥ al-Ayyūb (637-647/1240-1249). His square-in-a-circle style dirhams were about 67% pure[1]).

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[1]) Paul Balog, „The Coinage of the Mamlūk Sultans of Egypt and Syria," *A.N.S. Numismatic Studies No.* 12, New York, 1964. *Idem.*, "History of the Dirham in Egypt from the Fatimid Conquest until the Collapse of the Mamlūk Empire," *Rev. Numismatique*, III (1961), 109-146.

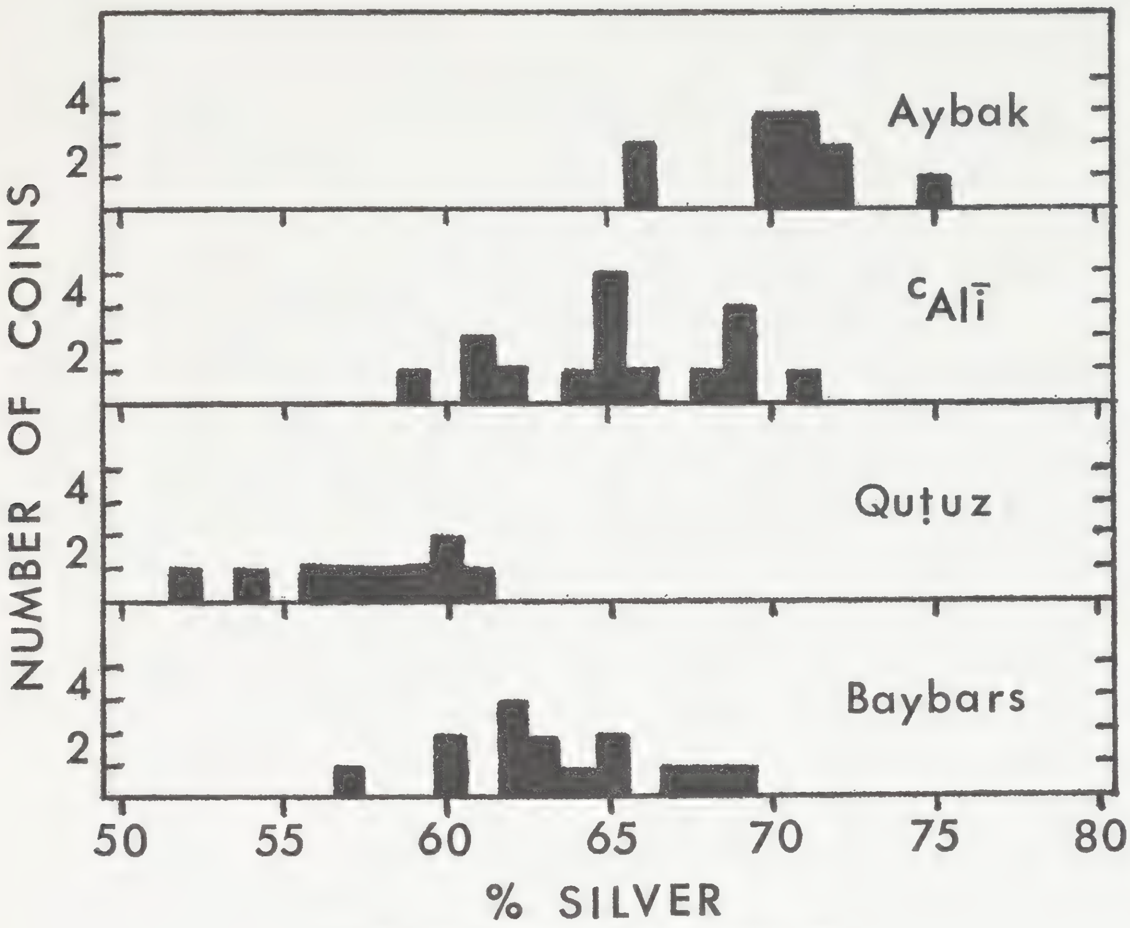

Fig. 2. Data for coins from four reigns

While Aybak and to a lesser extent ʿAlī, maintained the standard of fineness of the dirham, the decline in purity is very marked during the reign of Quṭuz. Quṭuz had to raise large sums of money in order to outfit a major expedition to fight the Mongols and under this tremendous economic and monetary pressure it is not unreasonable to postulate that Quṭuz deliberately lowered the fineness of his dirhams.

Although successful at the battle of ʿAyn Jālūt, 658/1260, Quṭuz was soon killed by the future sultan Baybars. NAA and destructive analysis of Baybars coins support the contemporary textual evidence

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1) Balog, *Rev. Num.*, p. 128.

concerning the purity of the coins [1]. Second, the differences which had appeared in the fineness of Syrian and Egyptian dirhams under the Ayyūbids permanently disappear. Finally, NAA tests help explain a major stylistic change which took place under Baybars. With the exception of a very few Ayyūbid style dirhams probably issued in 648/1260 Baybars' silver coins look different. In fact, they are famous for the first appearance of heraldic devices, such as the lion *passant* on his coinage. Was there a more dramatic way to indicate that his coinage was finer than the dirhams of Quṭuz than changing the style?

One device which modern Islamic historians use for estimating the purity of silver coins is to calculate the percentage of purity as a function of the contemporary gold: silver exchange rate. For most of medieval Egyptian history the rate of 1 : $13^1/_3$ is used as the basic relationship between a pure dīnār and pure dirhams. Thus, when the dirham is only $66^2/_3$ pure, the rate is 1 : 20. What happens to the exchange rate when the standard of the dirham is maintained but the fineness of the dīnār changed? To analyze this question, the reign of the Baḥrī Sultan Khalīl (689-693/1290-1294) was chosen. Noted primarily for the final expulsion of the crusaders from the Levant, the reign is important from a monetary point of view as one of the few times there is a decline in the fineness of the Mamlūk dīnārs [2]. While the purity of the gold issues fell, NAA tests as listed in the appendix, indicate that the fineness of Khalīl's silver coins was maintained at about $66^2/_3\%$. Since there is no textual evidence that the exchange rates varried from 1 : 20, we may conclude that these exchange rates are only a function of the purity of the dirham and can not be used to estimate the purity of the circulating gold coin.

The exchange rate of about 1 : 20 continued for the remainder of the Baḥrī period reflecting a degree of fineness of about 60-65%. In 789/1387 Barqūq (784-801/1382-1399), the first Circassian sultan, issued a new style silver coin. When his dirhams were tested for their purity, there appeared a slight drop in the standard as well as two coins as low as

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[1] *Ibid.*, p. 139 and Appendix.

[2] J. Bacharach, "The Standard of Fineness of Mamlūk Dīnārs," To be published.

27%. There was also an increase in the dīnār: dirham exchange rates at this time which may be associated with this debasement of the coin. Unfortunately there were no dirhams available for testing from the reign of Barqūq's son, Faraj (801-815/1399-1412) when the Arab chronicles record a complete debasement of the silver currency.

Dr. Balog established that a new small silver coin, first issued in large quantities in Egypt by Sultan al-Muʿayyad Shaykh (815-824/1412-1421) was over 90% pure and that a standard of about 95% was maintained by the Sultans Barsbāy (825-841/1422-1437), Aynāl (857-865/1453-1461), and Qāyitbāy (872-901/1468-1496) ¹).

Neutron activation analysis of these small, light dirhams produced similar results although the range of values was greater. The NAA tests included specimens from every major reign after Sultan al-Muʿayyad Shaykh as well as from the last decades of the Mamlūk rule when the economic situation had severely deteriorated, the gold coinage had been debased, the copper coins were the most abundant money and silver was extremely scarce. Thus a surprising result of these tests was that the dirhams of Sultan al-Qānṣūh al-Ghawrī (906-922/1501-1516), although very light, maintained a high degree of fineness. (See summary of data in Figure 3.)

Although Sultan Muʿayyad Shaykh was the first Circassian ruler to issue this new, light dirham in large quantities, he did not initiate the reform. According to the textual sources Shaykh's rival, the Amir Nawrūz (d. 817/1414) who was Viceroy of Syria in 815/1412 issued a new silver coin weighing half a dirham coin weight (ca. 1.41 grams). There has been a certain amount of confusion as to whether the Nawrūzī was the new standard for purity as well as for weight. Most modern scholars have accepted an estimation of 66²/₃% for the purity of the Nawrūzī ²). While a careful examination of all the available textual

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1) Balog, *Rev. Num.*, p. 139.

2) William Popper, "System Notes to Ibn Taghrī Birdī's Chronicle of Egypt," University of California *Pub. in Semitic Philology*, XVI (1957), 56. Ahmad Darrag, *L'Egypte sous le règne de Barsbay*, Damascus (1961), p. 100. Subhi Y. Labib, *Handelsgeschichte Ägyptens im Spätmittelalter*, (Wiesbaden, 1965), p. 427.

evidence can show that this Nawrūzī was a "pure" dirham rather than similar to the earlier Baḥrī issues ¹), NAA tests also proved it. Although only one specimen was available at the American Numismatic Society, it had a purity of 90%. Thus, the data acquired by modern techniques served as a check on the conclusions based on textual evidence. An example of an apparent disagreement between textual evidence and scientific analysis is the following. ²)

The historian Ibn Taghrī Birdī related that during the reign of Aynāl, in Rabīʿ I, 861/January, 1457, a crisis arose over the intrinsic value of Aynāl's dirhams, particularly those minted in Syria. In order to restore public confidence Aynāl ordered that an assay be run on the dirhams of Shaykh, Barsbāy, Jaqmaq and his own. The tests revealed that the first were 95% pure, the second and third 94½% and his Cairo issues 96% fine. When his Damascus and Aleppo issues were tested, they proved to be only 50% pure. The Sultan became angry and ordered the ceasing of the minting of the Syrian coins. They were not to be used in Cairo but turned into the mint. The populace was afraid that the Sultan would make a large profit by this action and, as was pointed out to the Sultan, the people could not distinguish between the Syrian and Egyptian coins as his name was on both. Under pressure the Sultan let the situation remain as it had been but within the year there appeared a rate for good silver and a rate for bad silver.

The account of Aynāl's assay allows us to judge the accuracy of our modern experiment as well as the awareness of the Arab historians of the purity of the dirhams. In both cases there was a high degree of correlation. The minor variations between the results of modern tests on individual coins and Aynāl's large scale test is a function of the history of each particular specimen analyzed and the methods employed.

However, there does appear a major contradiction between the written record of Aynāl's assay and modern tests. All the Syrian issues of Aynāl analyzed in the last few years exhibited a very high degree of

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1) al-Maqrīzī, *al-Sulūk*, MS (Cairo), Dār al-Kutub al-Miṣriyya, No. 339, Vol. IV, pp. 86-87.

2) Ibn Taghrī Birdī, *Ḥawādith*, Ed. William Popper, (Berkeley, 1931) pp. 294-296.

fineness, not the low percentage recorded in Ibn Taghrī Birdī's account. The variance between the two tests was not due to an error on the part of Ibn Taghrī Birdī but due to the nature of the sample tested by modern scholars. Aynāl's test took place in early A.H. 861 and the sample he must have used was minted from 857/1453 through 860/1456. In his catalog Balog listed only a few Syrian dirhams all from Damascus, which can be dated before A.H. 861 and there is no indication that those coins were tested for their intrinsic value. In the tests run at The University of Michigan only one of Aynāl's dirhams was dated before A.H. 861 and that was a Damascus issue dated A.H. 860 with a degree of fineness of 86%. While this was the lowest percentage for all the dated issues of Aynāl, it was not the 50% the chronicles spoke of. More pre-861 coins must be tested before we can conclude that the contemporary account might be inaccurate. There was another Damascus coin, undated, whose inscription for the mint varied from the other contemporary issues. The percentage of purity of the coin was only 8%. As the weight of the coin also varied significantly from the other issues of Aynāl, this particular coin was either an extreme debasement or more likely, a forgery.

There are textual data to prove that in Aleppo, in 861/1456, the production of the old dirham which was primarily composed of copper was replaced by new dirhams which were free from debasement [1]. As for Damascus, a similar change probably took place at about the same time although supporting textual evidence is lacking. Much later, in 877/1472, during the reign of Qāyitbāy, an assay was run un Damascus and the issues were found to be 95% pure [2].

The foregoing discussion has demonstrated the following: (1) The NAA method described here is superior to any other form of testing silver coins as it is completely non-destructive, safe, quick, and uses equipment found in most university chemistry departments, (2) the results are comparable to those achieved by destructive analysis, and

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[1] al-Tabbākh, *A'lām al-Nubalī bi-Ta'rīkh Halab,* (Aleppo, 1923), III, pp. 55-56.

[2] al-Jawharī, *Inbā' al-Haṣr fī Anbā' al-Asr,* MS (Paris), Bibliothèque Nationale, No. 1791, p. 193.

(3) the specific results can be correlated with textual evidence in order to explain monetary and economic developments. Therefore, as a tool for exploiting new and essential data from a major historical source, silver coins, the use of neutron activation analysis for determining the fineness of these coins can be an extremely important development.

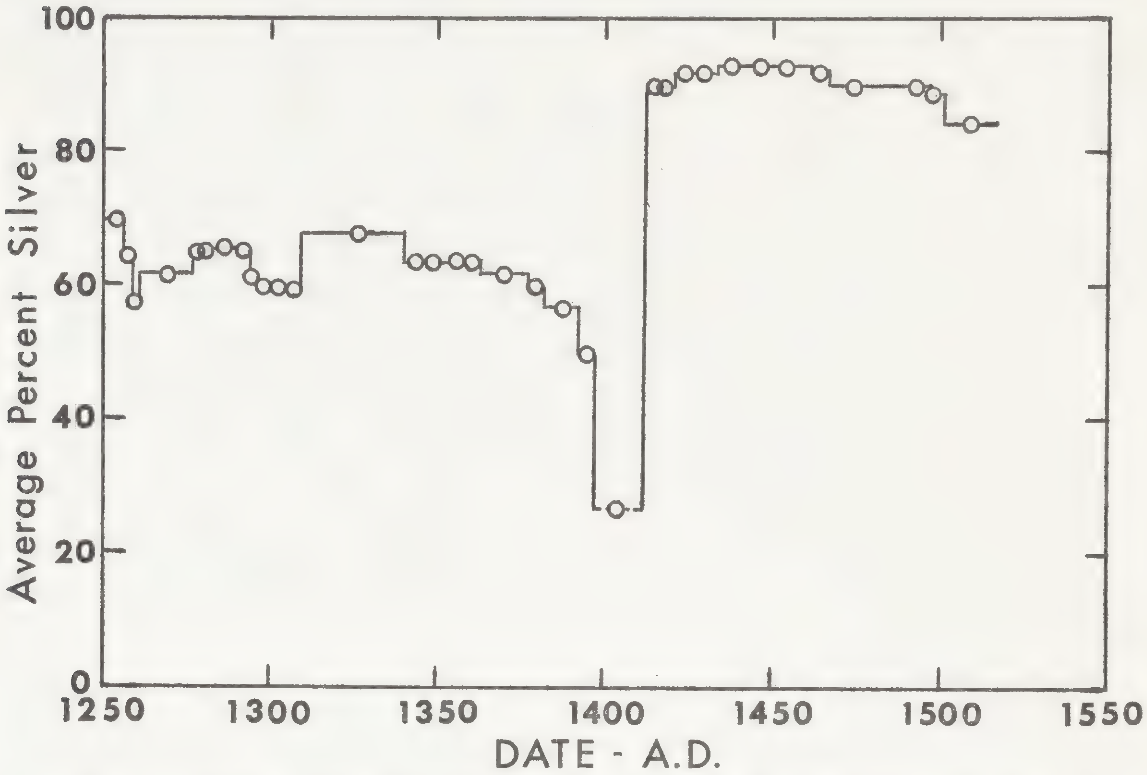

Fig. 3. Average silver content of coins issued by rulers during the period A.D. 1250-1517

APPENDIX

Percentage of Silver in Mamlūk Dirhams

I. *Baḥrī Sultans*

Mint	*Date*	*Weight*	% *Ag.*
Aybak (648-655/1250-1257)			
Cairo	653	2.92	71
Cairo	653	2.80	72
Cairo	653	2.83	71
Cairo	654	2.53	70
Cairo	65–	3.03	75
Cairo	65–	2.62	70
Cairo	65–	2.92	72
Cairo	65–	2.80	71
Cairo	65–	2.81	66
Cairo	65–	2.69	70
Cairo	65–	2.77	66

I. *Baḥrī Sultans*

Mint	*Date*	*Weight*	*% Ag.*
ʿAlī (655-657/1257-1259)			
Cairo	654	2.90	71
Cairo	655	2.74	69
Cairo	655	2.79	69
Cairo	655	2.88	65
Cairo	655	2.87	65
Cairo	655	2.81	68
Cairo	655	2.86	61
Cairo	655	2.82	65
Cairo	655	2.88	65
Cairo	655	2.81	66
Cairo	655	2.53	64
Cairo	655	2.85	69
Cairo	657	2.97	62
Cairo	657	2.88	59
Cairo	657	2.88	61
Quṭuz (657-658/1259-1260)			
Cairo	657	3.04	58
Cairo	657	2.92	61
Cairo	65–	2.79	60
Cairo	65–	2.95	60
Cairo	65–	2.85	56
Cairo	65–	2.45	59
Cairo	65–	3.00	57
Cairo	65–	2.99	54
Cairo	65–	2.75	53
Baybars (658-676/1260-1277)			
Cairo	658	2.65	57
Cairo	659	2.74	62
Cairo	659	2.44	65
Cairo	660	2.64	63
Cairo	664	2.80	63
Cairo	66–	2.82	65
Cairo	669	3.05	67
Cairo	67–	2.94	62
Cairo	6—	1.87	60
Cairo	667	3.50	62
Dam.	659	2.72	64
Dam.	667	2.91	68
—	—	2.95	69
—	—	3.76	60
Baraka Qan (676-678/1277-1279)			
Cairo	676	2.94	59
Cairo	677	2.24	67
Dam.	676	2.77	66
Dam.	677	2.94	67
Salāmish (678/1279)			
Cairo	678	3.33	68
Dam.	678	3.13	65
Qalāʾūn (678-689/1279-1290)			
Cairo	681	2.83	65
Cairo	685	2.94	65
Alex?	684	3.27	68
Hamah	689	3.59	68
Hamah	—	3.06	65
Dam.	68–	3.23	65
Dam.	68–	3.15	66
Khalīl (689-693/1290-1294)			
—	691	2.71	69
—	69–	2.93	68
—	69–	2.98	65
—	69–	2.74	66
—	69–	3.61	59
Kitbughā (694-696/1294-1296)			
Cairo	695	3.01	63
Cairo	—	2.97	61
Dam.	69–	2.97	59
Lājīn (696-698/1296-1299)			
Dam.	696	2.82	61
Dam.	696	2.92	56
Dam.	6—	3.08	56
Shaʿbān II (764-778/1363-1377)			
Cairo	—	—	65
Cairo	—	3.88	66
Cairo	—	1.88	41
Dam.	—	1.63	58
al-Manṣūr ʿAlī (778-783/1377-1381)			
—	—	2.31	59
—	—	3.41	70

II. *Circassian Sultans*

Mint	*Date*	*Weight*	*% Ag.*
Barqūq (784-791; 792-801/1382-1399)			
Cairo	789	2.26	58
Cairo	789	4.36	61
—	—	2.13	46
Cairo	789	1.59	55
Cairo	789	2.19	60
—	—	1.24	48
Cairo	789	1.98	27
Aleppo	—	2.87	57
—	—	1.85	27
al-Mustaʿīn Billāh (815/1412)			
—	815	1.02	90
al-Ṣāliḥ Muḥammad (824-825/1421-1422)			
—	82–	2.14	84
—	82–	2.30	88
Barsbāy (825-841/1422-1437)			
Dam.	—	2.25	86
Dam.	—	1.89	87
Dam.	—	1.94	66
Dam.	—	2 23	83
Dam.	—	2.02	87
Dam.	—	1.92	93
Dam.	—	2.01	89
Dam.	—	2.29	83
Dam.	—	2.24	92
Dam.	—	2.07	84
Dam.	—	2.19	88
Dam.	—	2.15	75
Dam.	—	2.27	85
Dam.	—	2.18	85
Dam.	—	2.13	84
Dam.	—	2.06	84
Dam.	—	1.80	93
Dam.	—	2.04	94
Dam.	—	2.07	93
Dam.	—	2.07	98
Dam.	—	2.05	89
Dam.	—	2.17	91
Dam.	—	2.21	90
Dam.	—	1.10	73
Dam.	—	1.04	91
Dam.	—	1.06	99
Dam.	—	0.93	83
Dam.	—	0.83	93
Dam.	—	2.18	85
Hamah	—	2.06	89
Hamah	—	2.09	90
Hamah	—	2.37	84
Hamah	—	1.88	89
Dam.	839	2.12	74
al-ʿAzīz Yūsuf (841-842/1437-1438)			
—	84–	2.21	94
Jaqmaq (842-857/1438-1453)			
Dam.	84–	1.72	92
Dam.	847	1.72	88
Dam.	84–	1.79	85
Dam.	84–	1.88	95
Dam.	84–	1.77	93
Dam.	84–	1.79	83
Aynāl (857-865/1453-1461)			
Cairo	86–	1.44	90
Aleppo	—	1.34	84
Aleppo	—	1.39	96
Aleppo	862	1.36	93
Aleppo	—	1.43	97
Aleppo	—	1.48	88
Dam.	860	1.49	86
Dam.	—	1.89	8
Dam.	862	1.49	91
Dam.	862	1.50	92
Dam.	—	1.47	91
Dam.	—	1.47	91
Dam.	862	1.43	93
Khushqadam (865-872/1461-1467)			
Aleppo	—	1.42	93
Aleppo	—	1.48	92
Aleppo	—	1.39	83
Qāyitbāy (873-901/1468-1496)			
Cairo	—	1.41	94
Cairo	—	1.47	89
Aleppo	—	1.45	81

II. *Circassian Sultans*

Mint	*Date*	*Weight*	% *Ag.*	*Mint*	*Date*	*Weight*	% *Ag.*
al-Nāṣir Muḥammad (901-904/ 1496-1498)				Al-Qānṣūh al-Ghawrī (906-922/ 1501-1517)			
Cairo	902	1.47	87	Dam.	—	1.18	80
—	—	1.34	91	Dam.	—	0.51	62
—	—	1.45	86	—	—	1.24	85
				—	—	1.45	82

ARCHAEOMETRY VOL. 10, 1967

QUANTITATIVE NON-DESTRUCTIVE NEUTRON ACTIVATION ANALYSIS OF SILVER IN COINS

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INTRODUCTION

Historians concerned with the ancient and medieval worlds have tended to rely solely on written evidence, neglecting the most abundant historical artifacts available—coins. When turning to numismatic evidence, the historian generally concerns himself only with the enscribed dates and names of rulers. However, the sheer quantity of coins available provides an opportunity for the historian, and particularly the economic historian, to study the coins for what they are—a money. In many cases coins are the most important, if not the only source of information about significant monetary and economic changes. Thus, the historian must go beyond the mere surface details of the coins, as valuable as these may be to him, and concern himself with the composition of the coins. Although the quantity of gold in gold coins can be approximated by determining the specific gravity, silver coins may be debased with varying amounts of lead so that the specific gravity measurements can be totally meaningless.

The elemental composition of probably no more than 1500 ancient and medieval coins have been reported in the literature. The reason is obvious; the analysis of the composition of a coin meant the destruction of an irreplaceable object. Even the use of small scrapings for spectroscopic studies has been limited because of the reluctance of curators and collectors to allow any permanent damage to the coins.

Neutron activation analysis, however, offers the possibility of making available to historians fundamental information about changes in the composition of coins without resorting to destructive analysis methods. Yet very little research on coins has been done using this technique. One of the most extensive studies using neutron activation analysis was performed at Oxford University where 500 5th century B.C. Greek silver coins were analysed for their copper and gold impurities (Emeleus 1958, Kraay 1959, Thompson 1960, Aitken et. al. 1962). Wyttenbach and Herman (1966) reported on the determination of the Cu and Ag contents of 400 15th century Swiss coins. Other studies include Norman and Suebic gold coins (Meloni and Maxia 1962), 3rd-8th century B.C. electrum coins from Lydia and Carthage (Das and Zonderhuis 1964, 1965), ancient Roman copper coins (Zuber 1966, Ravetz, 1963), 4th-6th century B.C. Greek silver coins (Bluyssen and Smith 1962), and recent Japanese silver coins (Kusaka 1959).

In the present study we have been concerned with the development of a rapid non-destructive method of analysis of the silver content of coins. We wished to base the analysis method on the short half-life isotopes of silver (^{108}Ag – 2.4 min, ^{110}Ag – 24 sec) and avoid producing appreciable amounts of the 270-day ^{110m}Ag isotope so that coins could be safely returned to their owners as soon as possible after performing the analysis. This requirement precluded the use of a nuclear reactor since the high neutron flux (10^{12} neutrons cm^{-2} sec^{-1}) would result in significant amounts of ^{110m}Ag unless the irradiation was limited to about 10^{-6} sec or the coins irradiated at a distance from the reactor where the flux was about

10^{-6} of that normally available in the usual irradiation positions. Physically, this latter possibility could pose problems in achieving reproducible positioning as well as rapid transfer of the coins from the reactor to the radioactivity detection equipment. Decreasing the irradiation duration to the time needed was impractical. An alternative irradiation procedure was used and the coins were irradiated instead using a Pu-Be neutron source.

NEUTRON SELF-SHADOWING EFFECTS

The use of the Pu-Be neutron source solved the problem of obtaining a low neutron flux. However, two effects which would also exist in reactor irradiations were still present. The large neutron absorption cross-sections of silver can lead to neutron self-shadowing effects. In addition, the high-energy neutrons, upon passage through the coin, become degraded in energy. Both of these effects result in data which were dependent upon the thickness of the coin. For example, the specific activity of various 90% silver (pre-1965) U.S. coins were found to be 464 for a 10c. piece (0.10 cm), 375 for a 25c. piece (0.13 cm), 303 for a 50c. piece (0.18 cm), and 223 counts/gm of silver for a silver $ (0.23 cm thick). For coins of equal thickness the specific activity was dependent on the silver content, but not in any simple direct way. A method of irradiation was devised which permits determining the silver content in three ways, one of which is independent of the thickness of the coin.

NEUTRON IRRADIATION

All irradiations described below were performed by placing the coin and a silver disk or an uncirculated (pre 1965, 90% silver) U.S. 10c. piece (taped to the back of the coin) about 1.5 inches from a 5 curie Pu-Be neutron source (figure 1) housed in a paraffin-filled Howitzer (Nuclear Chicago Corp., Model NH 3). At this position the thermal neutron flux was approximately 4 x 10^4 neutrons cm^{-2} sec^{-1} when the 1.5 inch space was filled with paraffin. The high-energy flux at this position was not measured but should have been much less than the thermal flux. The coin and silver disk were irradiated for 1.00 min. Under these conditions the only element present in a typical coin which would be sufficiently activated to be detected would be silver. No detectable amounts of the 270-day ^{110m}Ag were formed in the irradiation and only the 2.4 min—^{108}Ag and 24 sec—^{110}Ag were detected. Because of the short half-lives of these isotopes it was possible to re-irradiate a coin about 15 min after an irradiation and thus obtain a series of repeat analyses.

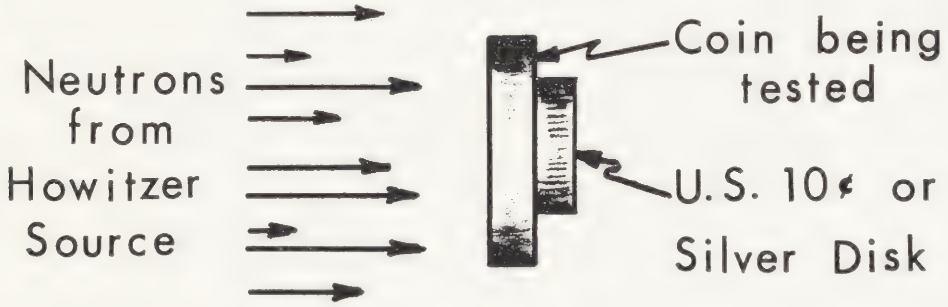

FIG. 1. The coin and a U.S. 10c. or silver disk taped to the coin are irradiated with neutrons.

COUNTING PROCEDURE

A 1.00 min count was taken on each coin starting 25 sec after the end of the irradiation. The coin was counted using a 2in x 2in. NaI(TI) scintillation detector shielded by 1 cm of plastic to absorb beta radiation. The detector was coupled to a single-channel analyser with the detection level set so that all activity between 0.16 and 0.70 MeV was recorded. Under these conditions very little of the beta activity of ^{108}Ag and ^{110}Ag was detected and essentially only decay gamma rays were recorded. Scintillation detection was chosen because it was possible to detect gamma-rays preferentially. If appreciable beta activity had been detected it would have been markedly dependent on the thickness of the coin because of beta-ray absorption within the coin. The silver disks or U.S. 10c. pieces were uniform in size and thickness and were counted by placing them 1 cm from a 3.2 mg/cm^2 end-window beta counter. This type of detector was chosen since the background activity was approximately 50 times less than that recorded by the scintillation detector. Appreciable beta-ray self-absorption occurred in the disk or 10c. pieces, but the uniformity of these silver backing pieces assured that the fractional self-absorption was constant in these two types of silver disks.

SILVER ANALYSIS

A number of modern U.S. and European coins of known silver contents (see Table I) were used in testing the validity of the methods of analysis. The data reported for these standards represent averages of 10 or more determinations.

TABLE I

ANALYSIS OF THE SILVER CONTENTS OF MODERN COINS

Coin	*Thickness cm.*	*Actual*	*Percent Silver Experimental*[a] *Eq.*1	*Eq.*2	*Eq.*3
1961 filed Mex. Peso	0.098	10.0	11.26	19.8	10.28
1961 Mexican Peso	0.198	10.0	9.76	23.7	10.25
1945 U.S. 5c.	0.173	35.0	34.4	33.1	33.4
1967 U.S. 50c.	0.175	40.0	32.9	44.7	39.2
1922 filed British ½ cr.	0.097	50.0	52.8	37.0	47.4
1930 British 6 pence	0.112	50.0	52.5	40.4	48.8
1929 British florin	0.196	50.0	42.8	53.7	49.0
1925 Austrian shilling	0.128	64.0	56.3	73.3	64.5
1944 Philippine 20 cent.	0.124	75.0	76.0	65.3	73.8
1951 Canadian 25c.	0.142	80.0	76.7	70.5	79.4
1886 Swiss franc	0.122	83.5	84.6	81.9	83.7
1964 filed U.S. 25c.	0.051	90.0	86.9	107.5	88.6
1964 filed U.S. 25c.	0.074	90.0	91.5	104.0	93.2
1964 filed U.S. 25c.	0.099	90.0	86.5	90.5	89.8
1908 U.S. 25c.	0.127	90.0	90.8	89.0	93.2
1944 U.S. 50c.	0.183	90.0	90.9	88.2	91.8
1882 U.S. $1.00	0.234	90.0	83.0	93.8	92.1
1918 Canadian 25c.	0.130	92.5	97.1	81.4	92.7
Pure silver	0.0084	100.0	70.8	49.0	63.9
Pure silver	0.017	100.0	86.1	62.1	77.7
Pure silver	0.025	100.0	89.4	121.2	87.3
	Average % Deviation[b]		8.0%	23.7%[c]	2.1%

[a] Experimental values based on average of 10 or more analyses.
[b] Pure silver data omitted in calculating % deviation.
[c] Average % deviation = 12.0% if Mexican Peso data omitted.

Method 1:

It might be expected that the logarithm of the activity per gram of silver in the coin would be proportional to the thickness of the coin, or more properly to the coin thickness times the silver percentage of the coin. However, a plot of the data according to this exponential relationship exhibited distinct curvature. A linear relationship provided a much more linear fit as seen in figure 2.

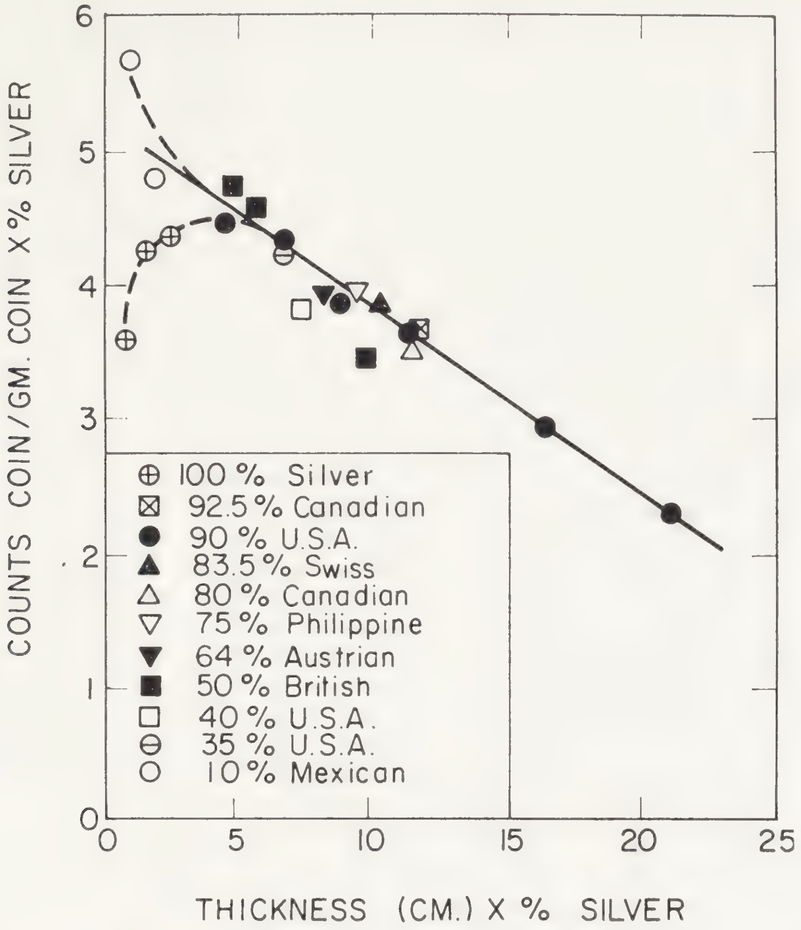

FIG. 2. Activity per gm. of silver in the coin as a function of thickness × % silver of the coin. Each data point is an average of 5 or more determinations.

The relationship implied by the data of figure 2 involves a quadratic expression in the percent silver in the coin.

The equation is:

$$AtmP^2 - BmP + C = 0 \qquad (1)$$

where A and B are constants determined from figure 2, t is the thickness, m the mass of the coin, P the % silver, and C the activity.

This method of analysis is very similar to that described recently by Wyttenbach and Herman (1966).

Attempts to use equation 1 for the analysis of the silver content of coins resulted in calculated silver percentages that varied widely for repeat determinations on the same coin as seen in Table II. This difficulty arises not only from uncertainties in the fit given in figure 2 but also from the difficulty in measuring accurately the

TABLE II

REPRODUCIBILITY OF REPEAT ANALYSES[a]

Counts in coin	*Counts in disk*	*Basis for Calculation* *Method 1*	*Method 2*	*Method 3*
696	300	120	57	94
657	330	94	38	81
663	323	110	42	83
734	342	130	29	87
589	274	91	77	87
573	250	88	98	93
690	301	120	57	93
Average:		107 ± 6	57 ± 9	88 ± 2

[a] Islamic coin, ca. 1450 A.D., 1.415 gm., 0.104 cm. thick.

thickness of ancient and medieval coins. These coins frequently are very irregular in thickness and it is often difficult to measure the thickness to an accuracy better than ±10%.

Even the silver content of modern coins cannot be determined too accurately by this method. Using the straight line of figure 2 as a general calibration to obtain A and B in equation 1 each coin was treated as if its composition was unknown and the silver content calculated using equation 1. These calculated percentages are given in Table 1. The average % deviation in the calculated silver content was 8%.

Method 2:

A simpler relationship is found if the coin to be examined is treated as an absorbing medium and the number of neutrons which penetrate through the coin determined. Rather than use a neutron detector to determine the neutron absorption of the coin we used instead standard silver disks taped to the back of the coin being irradiated. The larger the number of neutrons absorbed in the coin, the smaller the number of neutrons that reach the disk. The silver disks, therefore, can serve in a manner analagous to that of a photocell in a spectrophotometer and the activity induced in the silver disks would be directly proportional to the number of neutrons that penetrate through the coin. If the coins to be analysed were sufficiently large, U.S. 10c. pieces were used as the "photocell" disks. For smaller coins, a series of pure silver disks were used.

Data obtained with the use of the various standard coins are given in figure 3. The standard curve of figure 3 is easier to work with in determining the silver content of a coin than is the relationship given by equation 1. The equation of figure 3 is:

$$\log I/C = -StP \qquad (2)$$

where I is the extrapolated straight-line intercept and S the slope of figure 3, C the activity, t the thickness, and P the % silver.

Equation 2 still has one important disadvantage; the thickness of the unknown coin figures prominently in the calculation. Thus, the uncertainty in the calculated silver content would be directly related to the uncertainty in the measurement of the thickness of the coin as well as the uncertainty in the fit of the curve of figure 2. Using values of I and S obtained from figure 3, values of P were calculated for repeat determinations on a single coin (Table II). Calculated values of P for the standards (Table I) also showed large errors, especially for the thinner coins and coins of lower silver content.

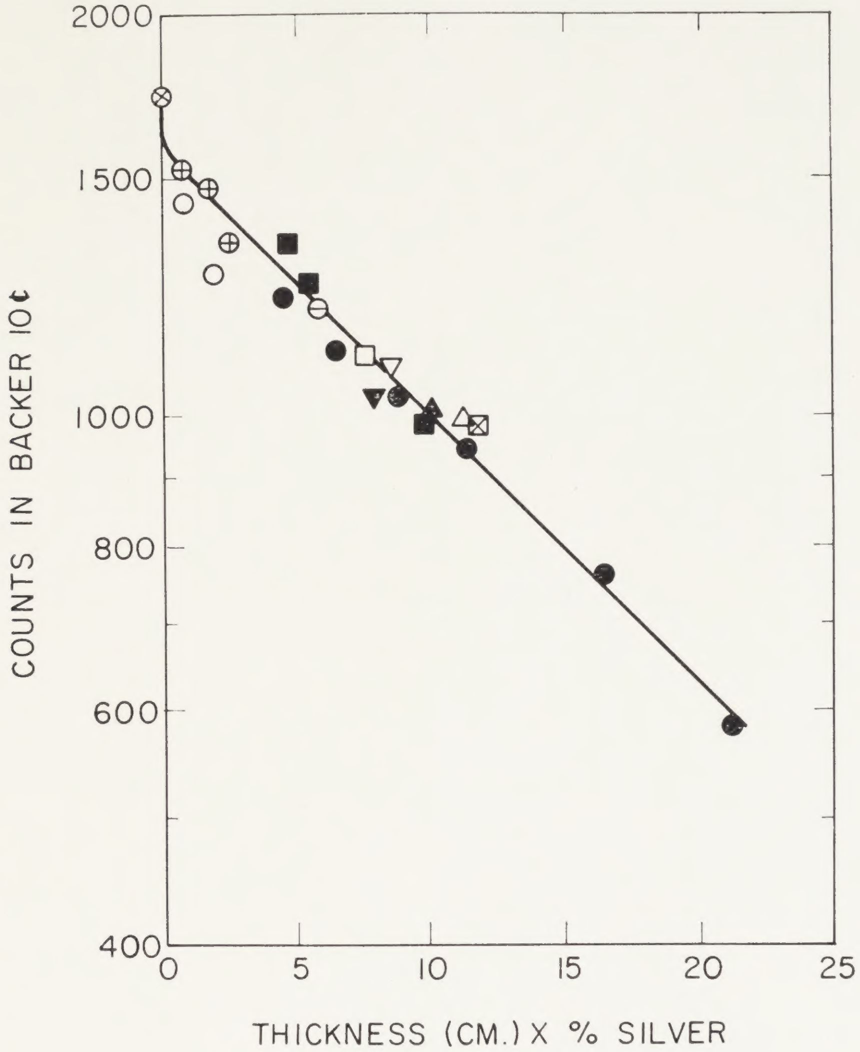

FIG. 3. Activity in U.S. 10c. backer disks as a function of the thickness × % silver of the front coin. Refer to figure 2 for identification of data. Point at zero thickness is for an unshielded 10c. disk.

Method 3:

However, an empirical relationship was found which was independent of the thickness of the coin over a wide range of thicknesses. It was found that the ratio of the activity per gm. of coin per % silver divided by the activity in the silver backer disk was a constant as shown in figure 4. Mathematically:

$$P = C_C/C_D mE \qquad (3)$$

where C_C and C_D are the activities of the coin and disk (or 10c. piece), respectively, m is the mass of the coin, P the % silver in the coin, and E the constant of figure 4.

The range over which this equation is valid encompasses the thicknesses of virtually all known ancient and medieval coins. A similar plot, which was a constant over the same thickness range, was found using the small silver disks. It is important to note that the data of figure 4 are plotted as a function of the coin thicknesses and not the coin thickness x the % silver, as in figure 2 and 3. Thus, the downward curvature at the left side of figure 4 is due to a thickness effect and not related to the silver content. If the silver content was important then the data

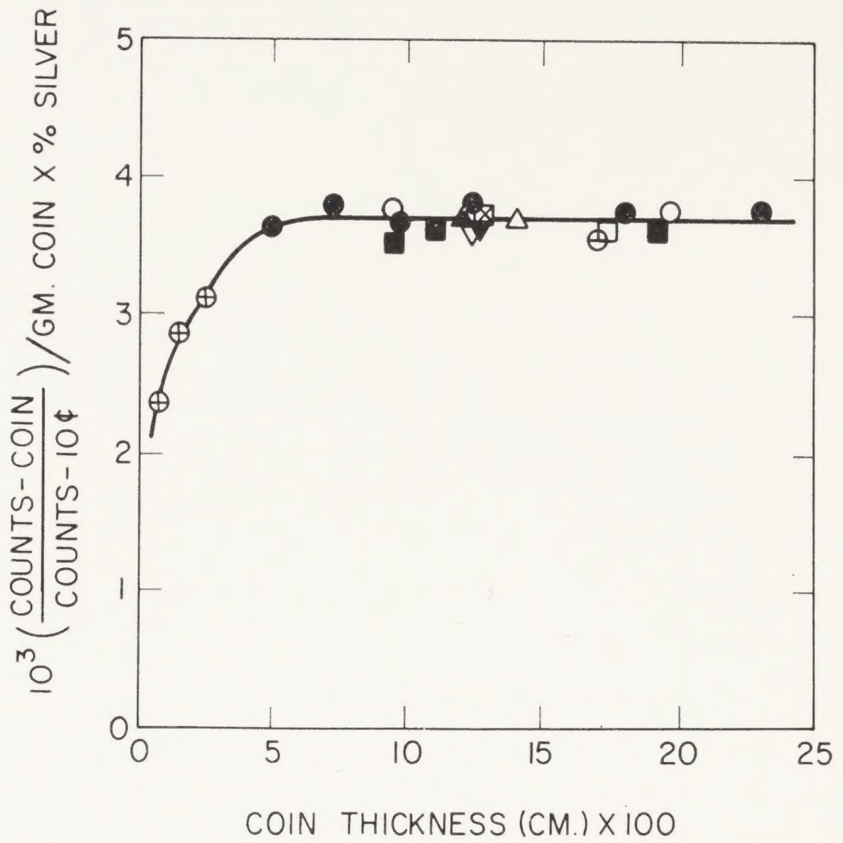

FIG. 4. Ratio of the activity per gram of silver in the coin to the activity in the 10c. backer disk as a function of the coin thickness. Data identification given in figure 2.

obtained for the 10% silver (Mexican) coins would have been numerically less. The ratio in the linear region (0.05 to 0.23 cm) of figure 4 is $(3.71 \pm 0.02) \times 10^{-3}$. Using this value, it should be possible to determine the silver content of an unknown coin to with ±0.5%. However, this accuracy is not achieved in a single determination since the counting statistics are rather poor, particularly for the unknown coin. Thus, about five analyses were made for each coin and the calculated percentages averaged. These average data were typically within ±2% of the actual silver content of the coins as in Table I. This accuracy is usually sufficient since ancient and medieval mints did not have "quality control" methods perfected to better than ±2%.

There are two reasons why determinations based on figure 4 should be more consistent than those based on figures 2 or 3. The first is the thickness independence of the ratio. The second is the (partial) cancellation of some systematic and random errors. Such errors could arise due to variations in positioning the coins during the irradiation and to slight variations in the timing of the irradiation or in beginning the one-minute count. Since these variations would be the same for both the coin and the backer disk the effects would tend to cancel and the ratio be more constant than the individual data for coin or backer disk. Using the value of the constant given in figure 4, the silver contents of the standards were calculated (Table I) and found to have an average % deviation of only ±2.1%.

An independent check of Method 3 was made using a series of Islamic coins for which the silver contents were also determined chemically. These coins were chosen for this analysis because they represented a set of "worst case" samples.

These particular coins had thicknesses which were about 0.13 cm. However, their diameters were quite small (about 1 cm) and the induced activity in each coin (about 500 counts) was relatively small compared with the background radiation of 1400 counts per min. The activities in the silver backing disks were about 300 counts compared with a background rate of 30 counts per min. Given in Table III are data obtained for four such coins using the activation analysis method according to equation 3 and, afterwards, a destructive chemical silver analysis. As is seen from these data, the agreement between the two methods is generally within ±2%.

TABLE III

COMPARISON OF SILVER CONTENTS

Coin	*Percentage Silver*	
	Activation Analysis[a]	*Chemical Analysis*
U.S. 10c.	(90)[b]	89.9
Canadian 10c	(80)[b]	80.2
Islamic	86 ± 2	87.7
Islamic	89 ± 2	93.1
Islamic	93 ± 2	93.5
Islamic	91 ± 2	92.1

[a] Based on Eq.3. Data are average of 5 or 6 analyses.
[b] Known silver content.

To date we have analysed over 800 coins using method 3. Data on Islamic coins from the Mamluk period have been reported by Bacharach and Gordus (1968). Representative data from this period are shown in figure 5. Other coins that were

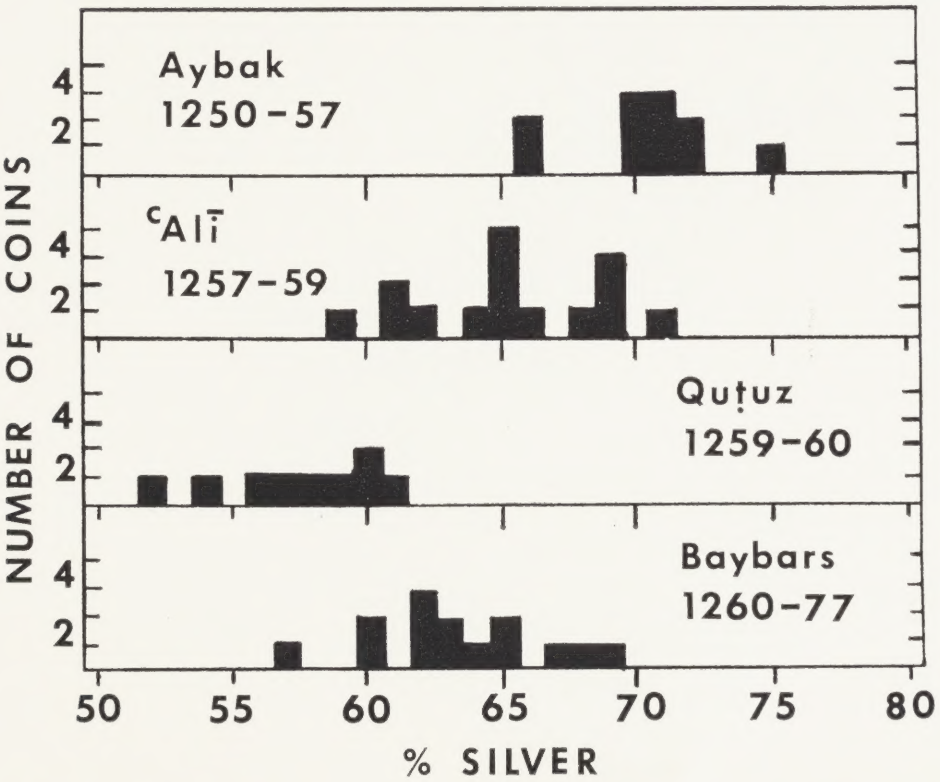

FIG. 5. Data obtained from the analysis of 49 Islamic coins from the period 1250-1277 A.D.

analysed include Sasanian silver and potin (Bacharach and Gordus, in press), Frankish Greek coins, and a hoard of 198 Ilkhanid dirhems of Uljaitu. In addition, the silver contents of a few gold and copper coins were also determined using method 3, which, it should be noted, is equally applicable to these types of coins.

ACKNOWLEDGEMENTS

Prof. Jere Bacharach originally suggested to the author the need for a simple non-destructive method of silver analysis. He provided many of his own coins for analysis and contributed the specimens that were destroyed for the chemical analyses. Dr. G. C. Miles of the American Numismatic Society arranged for the loan of Islamic and Sasanian coins and Prof. D. M. Metcalf of the Ashmolean Museum lent Frankish Greek coins. John Secrist, Barry Bateman, and Glenn Woodsum, Honors undergraduates at The University of Michigan, assisted in developing the methods and performing the analyses. This study was supported by a grant from the University of Michigan—Memorial Phoenix Project and by the U.S. Atomic Energy Commission, Division of Research.

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